NIST–JANAF Thermochemical Tables for the Bromine Oxides

Malcolm W. Chase
Standard Reference Data Program, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Received July 25, 1995; revised manuscript received May 1, 1996

The thermodynamic and spectroscopic properties of the bromine oxide species have been reviewed. Recommended NIST–JANAF Thermochemical Tables are given for six gaseous bromine oxides: BrO, OBrO, BrOO, BrOBr, BrBrO, and BrO_3. Sufficient information is not available to generate thermochemical tables for any condensed phase species. Annotated bibliographies (over 280 references) are provided for all neutral bromine oxides which have been reported in the literature. There are needs for additional experimental and theoretical data to reduce the uncertainties in the recommended values for these six species. Of all the species mentioned in the literature, many have not been isolated and characterized. In fact some do not exist. Throughout this paper, uncertainties attached to recommended values correspond to the uncertainty interval, equal to twice the standard deviation of the mean. © *1996 American Institute of Physics and American Chemical Society.*

Key words: bromine oxides; evaluated/recommended data; literature survey; spectroscopic properties; thermodynamic properties.

Contents

List of Tables

1. Introduction

As a continuation of previous studies which dealt with the thermodynamic properties of the chlorine oxides[1] and oxygen fluorides,[2] this study deals with the neutral bromine oxides. A succeeding article will deal with iodine oxides. We will not discuss the astatine oxides, as there appears to be only an estimated D_0° value reported in the literature for AtO(g). Specifically, this study examines the thermodynamic properties of the neutral oxides, not the gaseous ionic and aqueous ionic species. The main purpose of this article is to

©1996 by the U.S. Secretary of Commerce on behalf of the United States. All rights reserved. This copyright is assigned to the American Institute of Physics and the American Chemical Society.
Reprints available from ACS; see Reprints list at back of issue.

generate thermochemical tables for bromine oxide species. In general, there are scant data available for the description of the spectroscopic and thermodynamic data for any of the bromine oxides, except for BrO, OBrO, and BrOBr. Although the prime emphasis was on the diatomic and triatomic species, a thorough search of all bromine oxygen species was conducted to decide which species had sufficient data.

For the time period 1907 to 1994, there are only 280 citations in Chemical Abstract Services (CAS) dealing with all phases of the bromine oxides; of these 147 deal with BrO, 45 deal with OBrO, and 25 with BrOBr. Of the approximately 25 oxides mentioned in the literature, however, there is not conclusive evidence as to the existence of all of them.

The major interest in the numerous bromine oxides is due to the important role these compounds play in stratospheric chemistry. For this reason, the spectroscopic characterization of these species is mandatory in order to explain possible reactions thermodynamically and kinetically and to monitor the species in real time. In addition, numerous researchers are examining bonding trends within all halogen oxide species. There are no commercial uses of the bromine oxides mentioned in the literature.

The current study is aimed at providing a complete and thorough coverage of the literature for spectroscopic and thermodynamic information. Although it is not the purpose of this article to summarize and critique the chemistry of the bromine oxides, all such references are provided here. The references were obtained primarily by use of commercial abstracting services and all NIST Data Centers. (Chemical Kinetics Data Center; Chemical Thermodynamics Data Center; Ion Kinetics and Energetics Data Center; Molecular Spectra Data Center; Vibrational and Electronic Energy Levels of Small Polyatomic Transient Molecules; Crystal and Electron Diffraction Data Center.) Since the literature survey revealed so few references in total for all neutral bromine oxides, all citations are listed in Sec. 10 (References Annotated Bibliography). It should be noted that the reading of the individual articles yielded additional references, many of which are included in the attached bibliography. Not included are those articles or books (textbooks and handbooks) which are simply presenting a summary of properties, with no critical evaluation. Note that the earliest reference for any bromine oxide species was in 1928. Even though many of these citations are not relevant to this study, future investigators will not have to search the past literature, but simply concentrate on the publications since 1994.

The current version (1985) of the JANAF Thermochemical Tables[3] does not include any bromine oxygen species, whereas the 1989 version of the Thermophysical Properties of Individual Substances[4] only includes BrO(g), for which 14 references are given; the latest of these being dated 1975. This latter critical review referred to data from four spectroscopic studies, two microwave studies, three EPR studies, four dissociation energy studies, and two earlier reviews. There are sufficient new data available to warrant a revision to this tabulation. The NBS Thermodynamic Tables[5] and its Russian counterpart by Glushko and Medvedev[6] listed values (C_p°, H°, S°, and $\Delta_f H^\circ$) at 298.15 K for BrO(g), but only an enthalpy of formation for BrO_2(cr). [The NBS Tables also listed values for three aqueous ions, Glushko and Medvedev listed two aqueous ions.] It should be noted that the NBS study was performed in 1964 and the Russian study in 1965, and were based on the same references.

There are many NASA-JPL publications on chemical kinetics in which enthalpy of formation tables are given. Of all the bromine oxides, only BrO(g) is listed by NASA-JPL.[7] These data are presented without citation or reference to the original source. Most of the recommendations are based upon data in the IUPAC Evaluation (Atkinson *et al.*, 1989,[8] 1992[9]). Some of the values are different from the current IUPAC recommendations, reflecting recent studies that have not yet been accepted and incorporated into that publication. IUPAC cites the origin of their values. All citations given by IUPAC are included in this article.

Lewis[10] in 1932 reviewed the kinetics of reactions that proceeded with velocities ranging from the flammable region to detonation. As part of this review the author summarized the kinetics of the explosion of ozone as sensitized by bromine. Lewis raised the question as to the possible formation of bromine oxides.

In a 1963 review article, Schmeisser and Brandle[11] summarized the data pertaining to the properties and chemistry of the halogen-oxide compounds. Although these authors did not discuss BrO, they examined BrOBr and OBrO in detail. A measured enthalpy of formation of OBrO(cr) was noted. Brief mention was made of BrO_3, Br_2O_5, and Br_3O_8, although it was clear that the authors were not convinced that these "compounds" existed.

A 1972 review by Brisdon,[12] discussed seven bromine oxide species: BrO, OBrO, BrOO, BrO_3, BrOBr, Br_2O_2, and Br_2O_4. Whereas there was a complete spectroscopic characterization of BrOBr presented, only a partial identification of BrO was made. General comments proposing the existence (or nonexistence) of the remaining compounds were made.

Clyne and Curran[13] surveyed the reaction kinetics of halogen atoms, excited molecular halogens, and halogen oxide radicals. The authors covered the literature through early 1976. Their discussion provided a summary of the bimolecular reactions of ClO and BrO with a variety of species. In the case of BrO, one of the products formed was BrOO. Thermodynamic enthalpies of reaction given in this review were extracted from earlier studies by Clyne.

Bromine and its oxides were reviewed (through 1992) by Keller-Rudek *et al.*[14] for the Gmelin series. An earlier review by Kotowski *et al.*[15] for this series was published in 1931. The Keller-Rudek review discussed in detail many oxides [BrO, BrO_2, BrO_3, Br_2O, BrBrO, Br_2O_2, Br_2O_3, Br_2O_4, Br_2O_5, and Br_2O_6], but only briefly mentioned others [BrO_4, BrO_6, Br_2O_7, Br_3O_8, Br_4O, Br_4O_2, and Br_4O_4]. Four species were listed in this review for which we do not have bibliographies. Two of these species [Br_4O, BrO_6] were stated to be weak complexes, whereas the other two [Br_4O_2, Br_4O_4] were assumed to be unstable intermediates.

On the other hand, this JPCRD article mentions two species [BrOO. $O_2BrOBrO$] which were not discussed by Keller-Rudek *et al.*[14]

[After this article was written and reviewed, we became aware of the existence of another review article by Wayne *et al.*[21] This article provides discussion on the thermodynamic and spectroscopic data on many bromine oxides. Although not of importance for our purposes, the article also discusses many other topics, including photochemistry and kinetics.]

In reading Sec. 5, the reader will soon learn that the existence of many of the bromine oxide compounds is questionable. The thermal instability of the bromine oxides has led to numerous difficulties in characterizing specific bromine oxides. The syntheses are not always reproducible. The following summarizes our interpretations of the probable existence of the compounds mentioned:

Exist and have been observed: BrO; OBrO; BrOO; BrOBr; BrBrO

Postulated: BrO_3; BrO_4; BrO_6; Br_2O_2

Observed as crystalline solid: OBrOBrO; $BrOBrO_2$; $O_2Br–BrO_2$; $O_2BrOBrO$; $BrBrO_4$; Br_2O_5

No conclusive confirmation as to existence: Br_2O_6; Br_2O_7; Br_3O_8; Br_4O; Br_4O_2; Br_4O_4

In the following discussions, analyses and calculations, the 1993 atomic weights of the elements[16] are used: A_r(Br) $=79.904\pm0.001$; A_r(O)$=15.9994\pm0.0003$. Since the mid-1950s, the relative atomic weight of oxygen has changed by 0.0006 to 15.9994. Similarly for bromine, the relative atomic weight has changed by 0.012 to 79.904. Relatively speaking, these changes are sufficiently small that we will not consider any conversions due to relative atomic weights.

In addition, the 1986 fundamental constants are used.[17] The key constant of interest in this work is the ideal gas constant: $R=8.314510\pm0.000070$ J mol^{-1} K^{-1}. In comparison to the 1973 fundamental constants,[18] R has changed by $+0.0001$ J mol^{-1} K^{-1}. The effect on the thermal functions with this change is $\Delta S°$ (298.15 K)$=0.004$ J mol^{-1} K^{-1} for OBrO(g) and BrOBr(g).

SI units are used for the final recommendations. Since we are dealing only with ideal gases and spectroscopic information. the resulting calculated thermodynamic tables refer to thermodynamic temperatures. Thus, no temperature scale conversions are necessary.

In the following discussions, the numeric values (and their uncertainties if given) presented are those reported in the original publication in addition to the SI value. This is to ensure quick confirmation of the extracted results and their uncertainties. These uncertainties (not always based on experimental and mathematical analyses) are the values quoted by the original authors and are often not fully described as to their origins. Our reported uncertainties for $S°$ and $\Delta_f H^0$ are calculated using a propagation of errors approach.

The recommended data presented in the NIST–JANAF Thermochemical Tables are a result of a combined appraisal of results from experimental studies, calculations (e.g. quantum-mechanical treatments) and estimations. All tables are calculated using the full significance of all numeric values. Rounding occurs at the end of the calculations. The uncertainty given represents our best attempt for twice the standard deviation.

The NIST–JANAF Thermodynamic Tables (Sec. 6) are calculated using the current atomic weights and fundamental constants, as well as the thermochemical tables for the monatomic and diatomic bromine and oxygen. These latter reference state thermochemical tables, as originally calculated, were based on the 1973 fundamental constants[18] and the 1981 relative atomic weights.[19] This will cause a slight offset in the formation properties of the order 0.01 kJ/mol; such an offset is well outside the uncertainty range of the enthalpy of formation of the bromine oxides. Neumann[20] has presented an identical thermochemical table for BrO(g); this table was prepared jointly with this author.[21]

1.1. References for the Introduction

[1] S. Abramowitz and M. W. Chase, "Thermodynamic properties of gas phase species of importance to ozone depletion," J. Pure. Appl. Chem. **63**(10), 1449–54 (1991).

[2] M. W. Chase, "NIST–JANAF Thermochemical Tables for the oxygen fluorides," J. Phys. Chem. Ref. Data **25**(2), 551–603 (1996).

[3] M. W. Chase, Jr, C. A. Davies, J. R. Downey, Jr., D. A. Frurip, R. A. McDonald, and A. N. Syverud, "JANAF Thermochemical Tables, 3rd Edition," J. Phys. Chem. Ref. Data **14**, Supplement No. 1, 1856 pp. (1985).

[4] L. V. Gurvich. I. V. Veyts, and C. B. Alcock, *Thermodynamic Properties of Individual Substances,* 4th ed., two parts (551 pp. and 340 pp.) (Hemisphere, New York, 1989).

[5] D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow. S. M. Bailey, K. L. Churney, and R. L. Nuttall, "The NBS Tables of Chemical Thermodynamic Properties. Selected Values for Inorganic and C_1 and C_2 organic substances in SI units," J. Phys. Chem. Ref. Data **11**, Supplement No. 2, 393 pp. (1982).

[6] V. P. Glushko and V. A. Medvedev, *Thermal Constants of Substances,* (145 pp.) (Academy of Sciences, Moscow, 1965), Vol. I.

[7] W. B. De More, S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina, "Chemical kinetics and photochemical data for use in stratospheric modeling," NASA-JPL Publication 92-20 (1992); this is one of a series of similar publications.

[8] R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, and J. Troe, "Evaluated kinetic and photochemical for atmospheric chemistry: supplement III," J. Phys. Chem. Ref. Data **18**(2), 881–1095 (1989).

[9] R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, and J. Troe, "Evaluated kinetic and photochemical for atmospheric chemistry: supplement IV," J. Phys. Chem. Ref. Data **21**(6), 1125–1568 (1992).

[10] B. Lewis, "Explosion in gases and their kinetics," Chem. Rev. **10**, 49–89 (1932); particularly pp. 72–5.

[11] M. Schmeisser and K. Brandle, "Oxides and oxyfluorides of the halogens," Adv. Inorg. Radiochem. **5**, 41–89 (1963).

[12] B. J. Brisdon, "Oxides and oxyacids of the halogens," Int. Rev. Sci.: Inorg. Chem., Ser. One **3**, 215–51 (1972).

[13] M. A. A. Clyne and A. H. Curran, "Reactions of halogen atoms, free radicals, and excited states," Gas Kinet. Energy Transfer **2**, 239–95 (1977).

[14] H. Keller-Rudek, D. Koschell, P. Merlet, U. Ohms-Brudemann, J. Wagner, and A. Wietchmann, "Bromine," System No. 7, Suppl. B2, *Gmelin Handbook of Inorganic and Organometallic Chemistry* (Springer, Berlin, 1992).

[15] A. Kotowski, R. Gagarin, M. du Maire, G. Glauner-Breittinger, W. Roman, A. Eisner, and F. Seuferling, "Bromine," System No. 7, Main Vol-

ume *Gmelins Handbuch der Anorganischen Chemie* (Verlag Chemie G.M.B.H., Berlin, 1931), 342 pp.
[16]IUPAC Commission on Atomic Weights and Isotopic Abundances, "Atomic weights of the elements 1993," J. Phys. Chem. Ref. Data **24**(4), 1561 (1995); Pure & Appl. Chem. **66**(12), 2423 (1994).
[17]E. R. Cohen and B. N. Taylor, "The 1986 CODATA recommended values of the fundamental physical constants," J. Phys. Chem. Ref. Data **17**(4), 1795 (1988).
[18]E. R. Cohen and B. N. Taylor, "The 1973 least-squares adjustment of the fundamental constants," J. Phys. Chem. Ref. Data **2**, 663 (1973).
[19]N. E. Holden and R.L. Martin, "Atomic Weights of Elements - 1981," Pure Appl. Chem. **55**, 1101 (1983).
[20]D. B. B. Neumann, "NIST–JANF Thermochemical Tables, Supplement 1995," J. Chem. Phys. Ref. Data, (submitted).
[21]R. P. Wayne, H. Poulet, P. Briggs, J. P. Burrows, R. A. Cox, P. J. Crutzen, G. D. Hayman, M. E. Jenkin, G. Le bras, G. K. Moortgat, U. Platt, and R. N. Schindler, "Halogen oxides: radicals, sources, and reservoirs in the laboratory and in the atmosphere," Atmos. Env. **29**(20), 2675–2884 (1995).

2. Chemical Species Coverage

The following is a list of all bromine oxide species cited in the Chemical Abstract Services (CAS) Indices (formula and substance). Aqueous ions and gaseous ions are not included in this study. The chemical name, formula, and CAS Registry Number (when available) are given. This list is complete through Volume 121 of Chemical Abstracts Services (December 1994). It is important to note that this listing gives species whose existence is now questioned. Deleted CA Registry Numbers are given to assure the reader that all past citations were retrieved. There is limited information on the existence of asymmetric isomers of the triatomic species—BrOO and BrBrO. Such asymmetric isomers exist for the chlorine oxides, although for the oxygen fluorides, FOO has been observed (but not FFO). (See Table 2.1.)

TABLE 2.1. Bromine oxide species.

		Chemical Abstracts and Registry	
Formula[a]	Name	Deleted #	Current #[b]
BrO	Bromine oxide	···	23878-08-2
BrO(BrO)	Bromine oxide	77968-12-5 16651-29-9 12233-84-0	15656-19-6
^{79}BrO (^{79}BrO)	Bromine oxide	···	24050-34-8
^{81}BrO(^{81}BrO)	Bromine oxide	···	23878-08-2
BrO_2 (OBrO)	Bromine oxide	···	21255-83-4
$^{79}BrO_2$ (O^{79}BrO)	Bromine oxide	···	29044-85-7
$^{81}BrO_2$ (O^{81}BrO)	Bromine oxide	···	29051-09-0
BrO_2 (BrOO)	bromodioxy	···	67177-47-3
BrO_3 (pyr)	Bromine oxide	26670-64-4	32062-14-9
BrO_4 (BrO_4)	Bromine oxide	56310-08-8	11092-92-5
Br_2O (BrOBr)	Bromine oxide	···	21308-80-5
$Br_2{}^{18}O$ (Br^{18}OBr)	Bromine oxide	···	21364-13-6
Br_2O(BrBrO)	Bromine oxide	···	68322-97-4
$^{79}Br_2O$ (Br^{79}BrO)	···	···	151921-01-6
$^{81}Br_2O$ (Br^{81}BrO)	···	···	151921-02-7
Br_2O_2 (BrOOBr)	Bromine peroxide	···	96028-01-2
Br_2O_3 (OBrOBrO)	Bromine oxide	55589-63-4	53809-75-9
Br_2O_3 ($BrBrO_3$)	Bromine bromate	···	152172-79-7
Br_2O_4 (Br(BrO_4))	Bromine perbromate	···	141438-65-5
Br_2O_4 (O_2Br–BrO_2)	Bromine oxide	···	53723-86-7
Br_2O_4 (O_2Br–O–BrO)	Bromine oxide	···	55589-64-5
Br_2O_5	Bromine oxide	···	58572-43-3
Br_2O_6	Bromine oxide	···	···
Br_2O_7	Bromine oxide	···	···
Br_3O_8	Bromine oxide	···	121992-88-0

[a]A secondary formula is intended to suggest the assigned structure. If there is no secondary formula given, this means that no structure has been determined for this species, but the atomic ratio is known.
[b]If no CA Registry Number appears in this column, the species is assumed *not* to exist.

3. Historical Perspective of the Bromine Oxides

It is informative to briefly summarize the types of studies which have been conducted through the years on the bromine oxides. Specific references are given in Sec. 9. This section is intended to simply highlight developments through the years, not to provide specific references.

Using the Chemical Abstracts Services Collective Indices as a backdrop for these historical comments, the period of 1907 to 1926 (the 1st and 2nd Collective Indices) revealed no citations for any bromine oxide species. Even the later citations do not refer to any studies in this time period or earlier.

In the time period 1927 to 1946 (the 3rd and 4th Collective Indices), Chemical Abstracts listed a total of ten citations dealing with bromine oxides. All citations can be grouped in two classes: (1) preparation of solid bromine oxides (from the reaction of bromine and ozone) and (2) preparation of Br_2O in CCl_4 solutions (from the reaction of bromine with HgO). It is not always clear whether the studies' prime motive was the preparation of bromine oxides or the decomposition of O_3. In all cases, the stability of the products was examined. The first citation (by Lewis and Schumacher in 1928) dealt with a study in which, upon mixing bromine and ozone in a flask (no temperature specified), a white deposit appeared. Soon thereafter, an explosion destroyed the apparatus. With such an auspicious debut, further studies of the bromine reaction with ozone were performed more carefully and at lower temperatures (15 °C).

For the time period 1947 to 1961 (the 5th and 6th Collective Indices), 16 additional articles were indexed in Chemical Abstracts Services. Again, this work concentrated on the preparation of condensed phase bromine oxides and was more definitive as to the exact composition of the compound formed during a specified reaction scheme. In addition, the absorption spectra and dissociation energy of BrO(g) were reported, and the enthalpy of formation of BrO_2(cr) was measured.

For the time period 1962 to 1971 (the 7th and 8th Collective Indices), 37 references were cited. The dominant theme was the formation of a particular bromine oxide species through radiolysis, photolysis, or shock waves of solutions of bromates (BrO, BrO_2, BrO_3) and EPR studies of γ-irradiated crystalline bromates (BrO, BrO_2, BrO_3, and BrO_4). There was some additional information on the spectroscopic properties of BrO(g), BrO_3, and Br_2O.

In the time period of the 9th and 10th Collective Indices (1972–1981), there was considerable activity in the area of the study of the reaction and formation of various bromine oxides. In addition to the spectral studies on BrO(g), BrO_2, BrO_3, and Br_2O, many were published on the preparation, structure, and Raman spectra of many of the oxides (Br_2O_3, Br_2O_4, Br_2O_5) in the condensed phases. EPR studies on BrO, BrO_2, BrO_3, and BrO_4 were continued.

For the 11th and 12th Collective Indices (1982–1991), there were extensive studies of the formation and reaction of BrO (including many dealing with the kinetics) in the troposphere and stratosphere. Fortunately, there are numerous definitive studies of the spectroscopic properties of the triatomic oxides.

In the past three years there has been experimental studies in which BrO_2 and Br_2O have been observed in the gas phase. Additionally, more definitive studies have examined the crystalline oxides in an attempt to confirm the existence of some of the higher valence bromine oxides.

In summary, there are no heat capacity, enthalpy, or vapor pressure studies for any of the bromine oxides. There are a few articles which detail the preparation and report decomposition temperatures for the condensed phases. There is one direct experimental enthalpy of formation measurement for BrO_2(cr), one enthalpy of formation measurement for Br_2O(g), and one equilibrium study for Br_2O(g). The spectroscopic properties and dissociation energy for BrO(g) have been studied adequately, but the complete spectroscopic determination and enthalpy of formation values for any of the other bromine oxides is lacking. Except for Br_2O, not all vibrational frequencies have been observed for these oxides. The identification and characterization of the crystalline phase is not always definitive.

4. Summary of the Data for the Bromine Oxide Species

4.1 Spectroscopic Information

The construction of thermodynamic tables for polyatomic gas phase species requires a knowledge of the spectroscopic constants of the molecule including electronic energy levels and degeneracies, vibrational frequencies and molecular structure (including bond angles and bond lengths). This information is necessary for any low-lying excited electronic states, as well as the ground state. These data are obtained either from direct spectroscopic measurements, from theory, or by analogy with other similar chemical compounds. In some cases, theoretical quantum mechanical calculations are used. There is some spectral information available on a limited number of bromine oxides in the condensed phase. Recent gas spectroscopic studies reveal structural and vibrational frequency information for BrOBr and OBrO. However, relying on information from the fluorine and chlorine oxides, estimates can be made for the structure and spectroscopic properties of the asymmetric triatomic oxides, BrOO(g), and BrBrO(g).

For diatomic molecules, spectroscopic information on the electronic energy levels and vibrational-rotational structure is necessary. Experimental data of these types are available for BrO(g). Similar information on ClO(g) is available for comparison.

4.2 Thermodynamic Information

The literature survey revealed little or no information on the thermodynamic properties of any of the bromine oxides, except for BrO(g) which was derived from spectroscopic data. There is a reference for the enthalpy of formation for BrO_2(cr). Although not explicitly cited in Chemical Abstracts, there is a reference for the enthalpy of formation of BrO_3(g). There are, however, numerous citations as to the thermal stability of the various condensed phase oxides.

For the gas phase species, BrO(g) has dissociation energy information available so that an enthalpy of formation may be calculated. Only experimental formation information has been reported in the literature for Br_2O(g), but not for any of the other gaseous bromine oxides.

There are insufficient data available to permit the calculation of thermodynamic functions for the condensed phase of any of the bromine oxides. No heat capacity or enthalpy data are reported in the literature for any of these oxides. There are some ambiguous data for the melting of the various condensed phase.

5. Discussion of the Literature Data

The information is discussed in terms of the individual bromine oxide species. This is not to imply that all those species exist or have been isolated and characterized. For example, current information suggests that Br_2O_6, Br_2O_7, and Br_3O_8 do not exist, whereas compounds such as BrO_3 and BrO_4 have been proposed but have not been isolated. The proposed existence of the former three was based on a chemical analysis which is now known to be in error. The references for each of the following subsections are found in the References–Annotated Bibliographies (Sec. 9). The squib notation is used to denote the references. The squib is formed by taking the last two digits of the year and the first three letters of the lead two authors.

Early studies, prior to 1960, which deal with the bromine oxides fall into three categories: (1) the reaction of bromine with ozone at low temperatures (<-40 °C), (2) the bromine sensitized decomposition of ozone, and (3) the reaction of bromine with HgO. In the former case, depending on the temperature and relative concentration of the two gases, the products have been stated to be Br_3O_8, BrO_3, Br_2O_5, Br_2O, and BrO_2, all in the condensed phase. However, due to the instability of these oxides and the lack of definitive characterization of the crystals, it was not possible to clearly define the reaction and its products. Reproducibility appeared not to be commonplace. It was also stated that BrO_2 decomposed to Br_2O as the temperature was raised above -40 °C, with Br_2O_7 proposed as an intermediate. Since the actual chemistry is not of prime importance in this article, and the fact that the characterization of the compounds is not definitive, these articles will not be discussed or critiqued in detail in the sections dealing with these six species.

The early studies revealed the presence of condensed phase products which were stable only at low temperatures, typically below 15 °C. Three articles by Lewis and co-workers examined the reaction of ozone and bromine to form an unstable oxide which they interpreted to be $(Br_3O_8)_n$. Schwarz and co-workers examined reaction schemes which produced BrO_2, Br_2O, and Br_2O_7. Zentl and Rienacher and Brenschede and Schumacher prepared Br_2O by the reaction of bromine vapor on specially prepared HgO and HgO in CCl_4 solution, respectively. As already stated, these reaction schemes produced products which were unstable above approximately 15 °C. In fact, the species of presumed composition Br_3O_8 was found to be very unstable, explosively unstable. [This compound was later shown to be most likely BrO_3.] These early preparative reports gave no quantitative information, other than a temperature at which a (presumed) compound appeared to decompose. The reason for emphasizing these points is that, even to the present, most reaction schemes for any of the bromine oxides still rely on the reaction of bromine gas and ozone in the gas phase or solution. Isolation and characterization is difficult and has led to ambiguous results.

5.1 BrO

The references for BrO can be grouped into numerous categories. Although these categories are somewhat arbitrary, the intent is to provide the reader with a general understanding of the information available. For the purpose of this article, we will discuss only the spectroscopy, EPR, and dissociation energy studies; others may not be addressed as these do not necessarily provide sound thermodynamic information.

1. Spectroscopy:
   - Cross sections -
     [88WAH/RAV], [77VOG/DRE]
   - Microwave -
     [69POW/JOH], [72AMA/YOS], [74LOV/TIE], [80LOE/MIL], [81COH/PIC]
   - IR -
     [78TEV/WAL], [81MCK], [84BUT/KAW], [91ORL/BUR]
   - UV (emission) -
     [37VAI], [38VAI], [47COL/GAY]
   - UV (absorption) -
     [50HER], [58DUR/RAM], [58ZEE], [80LOE/MIL], [81BAR/COH], [85DUI/HUD]
   - Other -
     [72YAN], [73BYB/SPA], [73PAN/MIT], [74DHA/CLE], [74DHA/CLE2], [74TIS], [81DOR/MEH], [81GRO/LAU], [85POY/PIC], [88IGE/STO], [89BOW/BOY], [93MON/STI]
2. EPR -
   [66CAR/LEV], [67CAR], [67CAR/LEV], [67CAR/LEV2], [67CAR/LEV3], [67CAR/LEV4], [69CAR], [70CAR/DYE], [71MIL], [71BYF/CAR], [72ADL], [72BRO/BYF], [75DAL/LIN], [86BYB], [86BYB2]
3. Dissociation energy/IP/EA -
   [47COL/GAY], [48GAY], [50BRE/BRO], [50HER], [53BRE], [53GAY], [54COT], [58BRE], [58DUR/RAM], [63SCH], [65GLU/MED], [66VED/GUR], [68GAY], [68WAG/EVA], [69BRE/ROS], [70DAR], [77GLI], [77VOG/DRE], [78DUN/DYK], [79HUB/HER], [81BOH/SEN], [82WAG/EVA], [84SAU/TAT], [86GIN], [97BAS/GAV], [88IGE/STO], [88SIN], [88TYK], [89GUR/VEY]; [92GIL/POL], [94RUS/BER]
4. Formation/decomposition/reaction/detection -
   [40MUN/SPI], [60BRI/MAT], [60MAT/DOR], [61GUE/GOU], [62GUE/PAN], [63BUR/NOR], [64TRE/YAH], [66BUX/DAI], [68BUX/DAI], [70AMI/TRE], [70TOM/STU], [71KAU/KOL], [71OSL], [73DIX/PAR], [73PAR/HER], [74CAH/RIL], [77GIL/GAR], [77TAD/SHI], [78TEV/WAL], [80SEH/SUD], [80YUN/PIN], [86BRU/AND], [86KRE/FAB], [86RAZ/DOD], [86HIL/MCC], [89BAR/BEC], [90SOL], [91ARS/ZIV], [91JAD/LON], [91NEU/DOR], [91SZA/WOJ], [92FAN/JAC], [92MCC/HEN], [92WAT], [94ARP/JOH], [94COX/COX], [94GAR/SOL], [94HAU/PLA], [94INO], [94MAR/COR], [94POM/PIQ], [95FLE/CHA]
5. Kinetics -
   [70BRO/BUR], [70CLY/CRU], [70CLY/CRU2], [71CLY/CRU], [75CLY/WAT], [75RAD/WHI], [75WOF/MCE], [76CLY/MON], [76MOI/YUR], [77CLY/CUR], [77CLY/WAT], [79LEU], [79WAT/SAN], [80JAF/MAI], [80MOL/MOL], [80NIC], [80SAN], [81CLY/MAC], [81DON/ZEL], [81MEN/SAT], [81RAY/WAT], [81SAN/RAY], [81SAN/WAT], [82ANT], [82COX/SHE], [82COX/SHE2], [82FER/SMI], [83BUT/MOR], [82BAU/COX], [84CLA], [85BYK/GOR], [86BRU/STI], [86MCE/SAL], [86MOX], [86SAN], [86TUN/KO], [87ELO/RYN], [87HIL/CIC], [88BAR/SOL], [88BRU/TOO], [88HIL], [88HIL/CIC], [88SAL/WOF], [88SAN/FRI], [88TOO/AND], [88TOO/BRU], [89AND/BRU], [89ATK/BAU], [89ATK/BAU2], [89AUS/JON], [89FRI/SAN], [89KO/ROD], [89MEL/POU], [89SAN/FRI], [89SOL/SAN], [90DAN/CAR], [90PHI], [90POU/LAN], [90POU/LAN2], [90TUR], [90TUR/BIR], [91AND/TOO], [91BAR/BAS], [91LAN/LAV], [91MUR], [91TUR], [91TUR/BIR], [92POU/PIR], [92ROS/TIM], [92WAH/SCH], [93BRI/VEY], [93CUR/RAD], [93MAU/WAH], [93SAL/WOF], [93THO/DAY], [93WIN/NIC], [94CHI/CAR], [94THO], [94TOU], [94WEN/COH], [95THO/CRO]
6. Review -
   [48GAY], [50BRE/BRO], [53BRE], [53GAY],

TABLE 5.1.1. Rotational constants for BrO (B_0/cm^{-1}).

Source	^{79}BrO	^{81}BrO	Comments
58DUR/RAM	0.455	0.472	B determined by plotting $\nu_{R(J)}$ vs $(J-2)^2$
69POW/JOH	0.4277893 ±0.0000037	0.4260164 ±0.0000030	B_{eff}; microwave spectrum
72AMA/YOS	0.4277789 ±0.0000017	0.4260037 ±0.0000030	B_{eff}; reported in MHz; microwave spectrum
74TIS	0.4282 ±0.0005	0.4264 ±0.0005	Review
81COH/PIC	0.42960660 ±0.00000013	0.42782007 ±0.00000013	$B_{eff}(B_{e2})$; rotational spectrum
81MCK	0.42960660 ±0.00000013	0.42782007 ±0.00000013	B_{eff}; values taken from 81COH/PIC; held fixed in this spectral analysis;
	0.426278	0.424510	B_0 values
84BUT/KAU	0.42778722 ±0.00000007	0.42601182 ±0.00000007	$B_{eff}(B_0)$; states this values (from infrared and microwave data) to be same as that derived by 81COH/PIC
91ORL/BUR	0.42778706 ±0.00000025	0.42601176 ±0.00000011	derived from infrared measurements

[57RAM], [66VED/GUR], [68GAY], [69BRE/ROS], [70DAR], [74LOE/TIE], [74SCH], [77CLY/CUR], [79HUB/HER], [84BAU/COX], [84BUR/LAW], [84SAU/TAT], [89ATK/BAU]

Spectroscopic Information

The microwave data which result in rotational constants are summarized in Table 5.1.1.

Vaidya [37VAI, 38VAI] assigned a system of bands in the region 4000–4600 Å to the radical BrO. The compound was obtained in a flame of ethyl bromide burning with oxygen. Vaidya proposed a provisional vibrational analysis. Coleman and Gaydon [47COL/GAY] studied the emission of BrO in flames. A vibrational analysis yielded $\omega_e''=713$ cm^{-1} and $\omega_e''x_e''=7$ cm^{-1}. Zeelenberg [58ZEE], using flash photolysis techniques with four brominated compounds, observed an absorption spectra which was attributed to BrO. No vibrational analysis was provided.

Durie and Ramsay [57RAM, 58DUR/RAM] observed the absorption spectra of BrO during the flash photolysis of Br_2–O_2 mixtures. Twenty absorption bands were recorded in the region 2890–2550 Å. Rotational and vibrational analyses were performed, leading to values for r_0, and B_0, as well as ω_e and $\omega_e x_e$ values. Only approximate rotational constants were observed:

$$^{79}\mathrm{BrO} \quad B_0=0.455\ \mathrm{cm}^{-1} \quad r_0=1.669\ \text{Å}$$

$$^{81}\mathrm{BrO} \quad B_0=0.472\ \mathrm{cm}^{-1} \quad r_0=1.635\ \text{Å}$$

Durie and Ramsay adopted a mean value of $r_0=1.65\pm0.02$ Å. The authors were able to describe the absorption bands in the same vibrational scheme as used by 47COL/GAY for emission, with a slight adjustment in the numbering scheme. The vibrational analysis yielded $\omega_e=771.9$ cm^{-1} and $\omega_e x_e=6.82$ cm^{-1}.

Powell and Johnson [69POW/JOH] detected the microwave spectra of the gas phase BrO radical in the $^2\Pi_{3/2}$ ground state. They reported rotational constants $B_{eff}(^{79}\mathrm{BrO})=12824.80\pm0.11$ (0.42779 cm^{-1}) and $B_{eff}(^{81}\mathrm{BrO})=12771.65\pm0.09$ (0.42602 cm^{-1}). These results are in good agreement with the EPR measurements which are mentioned later in this section.

Using microwave detection techniques, Amano *et al.* [72AMA/YOS] determined the equilibrium structure and dipole moment of the gas phase BrO. They reported $B_{eff}(^{79}\mathrm{BrO},\ ^2\Pi_{3/2},\ v=0)=12824.49\pm0.05$ MHz (0.42779 cm^{-1}) and $B_{eff}(^{81}\mathrm{BrO},\ ^2\Pi_{3/2},\ v=0)=12771.27\pm0.09$ MHz (0.42600 cm^{-1}). The authors recommended $r_e=1.7171\pm0.0013$ Å for both isotopic species as derived from B_e.

Yanishevskii [72YAN] studied the relationship between vibrational frequencies and dissociation energies. No new data were presented.

Byberg and Spanget-Larsen [73BYB/SPA] used a modified extended Huckel method to calculate nuclear quadrupole coupling constants. No new structural information for BrO was provided.

Pandey *et al.* [73PAN/MIT] calculated the mean amplitudes of vibration of BrO at the temperatures $T=298.16$ and 500 K. The bond and molecular polarizabilities have been computed using the Lipincott–Stutman Δ-potential function model of chemical bonding.

Dhar and Cleveland [74DHA/CLE, 74DHA/CLE2] presented calculations relating the Morse-potential energy function with force constants, vibrational frequencies and dissociation energies. Calculations refer back to the Durie and Ramsay (1958) study. No new data were provided.

In their review of microwave spectra of diatomic molecules, Lovas and Tiemann [74LOV/TIE] recommended rotational constants and ground state splitting based on data from Amano *et al.* (1972). However, they also referred to the EPR results of [67CAR/LEV3] and [71BYF/CAR].

Tischer [74TIS] analyzed the $X^2\Pi_{3/2}$ spectrum of the BrO radical by calculating energy eigenvalues of the corresponding Hamiltonian. The author adopted [70CAR/DYE]'s EPR value of $B_0=0.4282$ cm^{-1} (^{79}BrO); $B_0=0.4264$ cm^{-1} (^{81}BrO) for the rotational constants and $A_0=-815\pm120$ cm^{-1} for the splitting of the two isotopic species (see the next section). An $r_0=1.7205$ Å (^{79}BrO) value was also quoted from [70CAR/DYE]. r_e values of 1.717 Å were likewise reported, based on the work of Amano *et al.* (1972) for both isotopic species.

Tevault *et al.* [78TEV/WAL] studied the reaction of atomic and molecular bromine with atomic and molecular oxygen in argon matrices (photolysis of bromine and ozone containing matrices). Several bromine oxygen compounds were stated to have been formed and identified by infrared spectroscopy—BrO, OBrO, BrBrO, BrOBr, and $(BrO)_2$. The authors assigned a very weak absorption at 729.9 cm^{-1} to BrO. The force constant calculated from this frequency was 4.18 mdyn/Å, a value which was not unexpected on the basis of the FO and ClO constants of 5.41 and 4.66 mdyn/Å respectively, obtained from their argon matrix frequencies. A reinterpretation of the data yielded $\omega_e=751$ cm^{-1} and $\omega_e x_e=5.0$ cm^{-1} for the ground state. The excited state was reported to lie at 27740 cm^{-1}.

Absorption spectra of BrO were observed from argon matrix samples prepared by microwave discharge of mixtures of argon, bromine and oxygen by Loewenschuss *et al.* [80LOE/MIL]. The authors reported an excited state of $T_e=26363$ cm^{-1} with $\omega_e=514.8$ cm^{-1} and $\omega_e x_e=4.8$ cm^{-1}. Vibrational constants for the ground state are $\omega_e=743.5$ cm^{-1} and $\omega_e x_e=6$ cm^{-1}. These values result from a reanalysis of earlier data and the current matrix work of [80LOE/MIL].

The absorption spectra and rotational analysis of the $A^2\Pi_i-X^2\Pi_i$ state of isotopically enriched ^{81}BrO and normal BrO have been obtained by Barnett *et al.* [81BAR/COH] using the flash photolysis of mixtures of bromine and ozonized oxygen. The authors quoted and used [81MCK]'s value of -968 cm^{-1} as the spin splitting in the ground state. The lower state rotational constants were taken to be those derived from the microwave study [81COH/PIC]. The rotational constants for the excited state were estimated as: $B'_3=0.314$ cm^{-1} and $\alpha'_e=0.0034$ cm^{-1}, with an internuclear distance of 1.95 Å. From the analysis of vibrational assignments for BrO, a value for $\Delta G''_{1/2}$ of 722.1 ± 1.1 cm^{-1} was obtained. Molecular constant values of $\omega''_e=730.6$ cm^{-1}, $\omega'_e=516.1$ cm^{-1}, and $D''_e=19\,694$ cm^{-1} were used for the calculations of the ν' and ν' bands.

Rotational spectrum of the $\nu=0$ and 1 bands and molecular parameters of BrO in the $^2\Pi_{3/2}$ state were observed by Cohen *et al.* [81COH/PIC]. Rotational constants for the $^2\Pi_{3/2}$ state were determined to be $B_{e2}=0.42960133$ cm^{-1} (^{79}BrO) and 0.42781482 cm^{-1} (^{81}BrO). The values of $\omega_{e2}=726$ cm^{-1} (^{79}BrO), 724 cm^{-1} (^{81}BrO) and $\omega_{e2}x_{e2}=4.92$ cm^{-1} (^{79}BrO), 4.90 cm^{-1} (^{81}BrO) derived from the mechanical constants were in good agreement with results obtained by [81BAR/COH], [78TEV/WAL] and [80LOE/MIL]. An r_{e2} value of 1.717263 Å was also determined for both of the isotopic species.

Doraiswamy and Mehrotra [81DOR/MEH] examined the collision-induced linewidths of BrO.

Grodzicke *et al.* [81GRO/LAU] calculated the dipole moment of BrO.

Using laser magnetic resonance spectroscopy on three CO_2 laser lines, McKellar [81MCK] detected magnetic dipole transitions between the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ components of the ground state of BrO. This was the first direct observation of the $^2\Pi_{1/2}$ state of BrO. A spectrum lying between 964.77 and 969.14 cm^{-1} was recorded for this state. The spin-orbit splitting parameter A and rotational constants $B^{\mathrm{eff}}(^2\Pi_{1/2})$ were determined to be -967.9831 cm^{-1} (^{79}BrO), -967.9981 cm^{-1} (^{81}BrO) and 0.4248 cm^{-1} (^{79}BrO), 0.4230 cm^{-1} (^{81}BrO), respectively. The author also predicted microwave rotational transition frequencies for the $X^2\Pi_{1/2}$ state of BrO.

Butler *et al.* [84BUT/KAW] observed the fundamental vibration-rotation band of the ^{79}BrO and ^{81}BrO radicals in the $^2\Pi_{3/2}$ ground electronic state (700–760 cm^{-1}) by using Zeeman-modulated IR diode laser spectrometry. The authors assigned a 721.92814 cm^{-1} value for the ^{81}BrO $A^2\Pi_i-X^2\Pi_i$ transition, which agrees well with the 714 cm^{-1} value estimated by [81COH/PIC] and the 722.1 ± 1.1 cm^{-1} value derived by [81BAR/COH] from optical spectra. Rotational constants $B_0=0.427781964$ cm^{-1} (^{79}BrO),$=0.426006591$ cm^{-1} (^{81}BrO), harmonic frequency $\omega_e=732.89$ cm^{-1} (^{79}BrO),$=731.37$ cm^{-1} (^{81}BrO), and vibrational anharmonicity $\omega_e x_e=4.74$ cm^{-1} (^{79}BrO),$=4.72$ cm^{-1} (^{81}BrO) were calculated. But based on the equilibrium spin-orbit coupling constant A_e, assumed to be independent of isotopic mass, the "true" $\omega_e=725.69$ and 724.18 cm^{-1} for the two isotopic species. The A_e value of -975.19 cm^{-1} (^{79}BrO) was based on the results of [82MAK/LOV] for ClO. The equilibrium internuclear distance was calculated from rotational constants to be $r_e=1.72072$ Å for both of the isotopic species.

Duignan and Hudgens [85DUI/HUD] reported the resonance enhanced multiphoton ionization spectra of ClO and BrO free radicals between 415 and 475 nm. BrO showed three new vibrational progressions starting from transitions between the $X\,^2\Pi_{3/2}$ state to Rydberg states with assignments of $E^2\Sigma$($\nu_{00}=65003$ cm^{-1}), $F^2\Sigma$($\nu_{00}=67470$ cm^{-1}), and an apparently inverted state, G($\nu_{00}=70504$ cm^{-1}). No doublet originating from the ground state $^2\Pi_{1/2}-^2\Pi_{3/2}$ spin-orbit splitting was observed. The authors proposed a ground state vibrational frequency of 714 cm^{-1}, obtained from the difference of the hot band at 466.51 nm and the E(0,0) band. This

TABLE 5.1.2. Rotational and electronic state splitting constants for BrO.

Source	Species	B_0/cm^{-1}	A/cm^{-1}	r_0/Å
66CAR/LEV	^{79}BrO	0.45		
	^{81}BrO	0.47		
70CAR/DYE	^{79}BrO	0.4282±0.0005	−815±120	1.720[a]
	^{81}BrO	0.4264±0.0005	−815±120	
71MIL	BrO	adopted values of [70CAR/DYE]		
72ADL	BrO	adopted values of [70CAR/DYE]		
72BRO/BYF	^{79}BrO	0.4281	−980	
	^{81}BrO	0.4263	−980	
81MCK	^{79}BrO	0.4278[b]	−967.983(2)	
	^{81}BrO	0.4260[b]	−967.9981(2)	

[a]Unspecified which BrO isomer (^{79}BrO or ^{81}BrO) it dealt with.
[b]These values are $B_{eff}(^2\Pi_{3/2})$.

value differed from the 722 cm^{-1} value proposed by [78TEV/WAL, 81BAR/COH, 84BUT/KAW], and the $F^2\Sigma$ (ω_e=822 cm^{-1}), $E^2\Sigma$(ω_e=897 cm^{-1}), and G^2($\Delta G_{1/2}$ =848 cm^{-1}) values for the Rydberg states. Values for $E^2\Sigma$($\omega_e x_e$ =2.6 cm^{-1}) were also given.

Poynter and Pickett [85POY/PIC] have created a computer-accessible catalog of submillimeter, millimeter and microwave spectral lines which was constructed by using theoretical least square fits to the observed spectral lines.

Ground-state properties of the fourth row main group monohydrides XH and monoxides XO (X=K through Br) were determined by Igel-Mann *et al.* [88IGE/STO] by means of self-consistent field/configuration interaction (SCF/CI) calculations. Bond lengths r_e=1.741 Å (3.29 a.u.), dissociation energy D_e=10646 cm^{-1} (1.32 eV) and vibrational frequency ω_e=726±10 cm^{-1} were calculated. The authors referred to the dissociation energy recommended by Huber and Herzberg (1979).

Wahner *et al.* [88WAH/RAV] measured the absolute UV cross section of BrO at 338.1±0.1 nm, the peak of the (7,0) band of the $A^2\Pi \leftarrow X\,^2\Pi$ transition. The absorption spectra of BrO in the wavelength range 312–385 nm were measured at 298±2 and 223±4 K using a flow tube reaction.

Bowmaker and Boyd [89BOW/BOY] performed a SCF-MS-Xα study of the bonding and nuclear quadrupole coupling in oxygen compounds with the halogens. Calculations were performed using structural information from [69POW/JOH].

The ν=1–0 band of BrO in the $X^2\Pi_{3/2}$ spin state was measured by Orlando *et al.* [91ORL/BUR] using high-resolution Fourier transform absorption spectroscopy. The values obtained were ν_0=723.414 (^{79}BrO) and ν_0 =721.927 (^{81}BrO). One hundred and thirty transitions were assigned and analyzed to determine the band origins and rotational constants of ^{79}BrO and ^{81}BrO. The BrO line positions were fit using the same expression as [84BUT/KAW]. The fits also included the microwave data of [81COH/PIC]. This fit involved the band origin rotational constant and centrifugal distortion constant. UV measurements recorded an $A^2\Pi$–$X\,^2\Pi$ transition of BrO in the region 285–355 nm (28169–35088 cm^{-1}). Rotational constants, B_0=0.42778706 (^{79}BrO) and B_0=0.42601176 (^{81}BrO) were also obtained. The molecular constants are in good agreement with those reported by [84BUT/KAU].

The photoionization spectrum of ^{79}BrO was measured by Monks *et al.* [93MON/STI] over the wavelength range λ=108–122 nm (81967–92593 cm^{-1}) using a dischargeflow photoionization mass spectrometry. The structure shown by the equivalent ^{81}BrO spectrum was indistinguishable. This is the first determination of the ionization energy for BrO($X^2\Pi_i$) to be obtained via direct photoionization threshold measurement, although it had been attempted by Dunlavey *et al.* [78DUN/DYK] earlier. A vertical excitation energy for the X→A transition was calculated (using MC-SCF method) to be 30539 cm^{-1} which compares favorably with an experimental adiabatic excitation energy 27926 cm^{-1}. This study also provides calculated values for three other excited electronic states. The authors quoted the three excited states of [85DUI/HUD]. An r_e=1.824 Å value was also proposed.

EPR Information

There are numerous EPR studies involving BrO. These studies can provide information as to the rotational constant (to yield an r_0 value) and the electronic spin orbit splitting constant (A), and are summarized in Table 5.1.2. In many of these studies this information has not been provided.

Carrington and co-workers have studied the EPR spectrum of BrO in the gas phase. In all cases there were difficulties in preparing the sample and observing the full spectrum due to the intensity of O_2 lines in the same region.

66CAR/LEV - A preliminary EPR study in which techniques for measurements were given for BrO. Eighteen lines of the 24 expected were detected, the remaining being obscured by the intense spectrum of O_2. The authors were confident that the spectrum arises from BrO ($^2\Pi_{3/2}$) in its lowest rotational level. The data were consistent with Duric and Ramsay's (1958) calculations for the rotational constant B_0=0.45 (^{79}BrO); =0.47 (^{81}BrO).

67CAR - A review article of EPR and other forms of microwave spectroscopy in which the BrO spectra was mentioned but no data was given.

67CAR/LEV - Attempted to study the EPR gas phase spectra of BrO. The relatively weak BrO lines were often obscured by the many intense O_2 lines which occur in the same field region.

67CAR/LEV2 - The effects of an electric field on the electron resonance spectra in the gas-phase were used to measure the dipole moment of BrO in its electronic ground state.

67CAR/LEV3 - Examined the EPR spectrum of BrO and detected double quantum transitions.

67CAR/LEV4 - A gas phase EPR cavity was developed which allows the application of a parallel Stark field. The spectra of BrO were observed clearly in the presence of O_2.

69CAR - High-resolution spectroscopic studies of the rotational levels of BrO. The author reviewed his previous studies involving the $^2\Pi_{3/2}$ electronic state of BrO.

70CAR/DYE - The gas phase EPR spectra of BrO in its $^2\Pi_{3/2}$, $J=3/2$ levels were described. The analysis confirmed that the radical has a $^2\Pi_{3/2}$ ground electronic state (8612.200 MHz). Values of the fine-structure splitting $A = -815 \pm 120$ cm^{-1} and rotational constant $B_0 = 0.4282 \pm 0.0005$ cm^{-1} (^{79}BrO); $=0.4264 \pm 0.0005$ cm^{-1} (^{81}BrO) were obtained. The determination of A as negative showed conclusively that the ground state was $^2\Pi_{3/2}$ (an inverted doublet). The authors favor their values over those obtained by 58DUR/RAM, leading to a calculation of $r_0 = 1.720$ Å.

Byfleet *et al.* [71BYF/CAR] measured the dipole moment of BrO using Stark splitting of the molecule's gas phase electron resonance spectra.

Miller [71MIL] reanalyzed the data from electron resonance experiments for BrO and IO. Although he stated that the splitting of the ground state was anomolously low for IO and questioned the treatment for BrO. he did not give a new value for the splitting of the ground state for BrO. Miller quoted the earlier results tabulated by [70CAR/DYE] for the spin–orbit coupling constant ($A = -815$ cm^{-1}).

Adl [72ADL] examined the EPR spectrum of gaseous BrO. He identified as the ground state a $^2\Pi$ electronic state for the radical where $J=3/2$. [72ADL] compares and contrasts ground and first excited rotational states of BrO, assigning the radical a spectra of 8775.5 MHz for both the ground state ($J=3/2$) and the excited state ($J=5/2$). The molecular parameters presented by [70CAR/DYE] were used to calculate the spectra for the $J=3/2$ and $J=5/2$ levels of BrO. No new parameters were presented by Adl.

The EPR spectrum of the gaseous BrO $J=5/2$ rotational levels of $^2\Pi$ ground state was observed by Brown *et al.* [72BRO/BYF]. A comparison with the results of $J=3/2$ levels lead to values for corrections. Spectra were recorded at 9720.26 MHz at $J=5/2$ levels using Stark modulation. This value, -980 cm^{-1}, is preferred to that of [70CAR/DYE] because of the more extensive data in the higher order data treatment method used by [72BRO/BYF] in comparison with that used by [70CAR/DYE].

Although secondary references imply that the article by [75DAL/LIN] deals with BrO, in fact it examines the EPR of BrO_2, BrO_4, and BrO_6 and is strictly a theoretical study.

Byberg [86BYB] studied the EPR of [XO, O_2], X=Br, Cl, formed from the decomposition of ClO_3^- and BrO_3^- in solid $KClO_4$:$KBrO_3$. The main features of the spin Hamiltonian [BrO, O_2] correspond to BrO ($^2\Pi$) in a crystal field, coupled through an isotropic exchange interaction to O_2 ($^3\Sigma_g^-$) to form a spin-doublet ground state. Hamiltonian values were given as experimental and calculated values at 26 K. Molecular hyperfine parameters in MHz for ^{79}BrO in the gas phase were also given.

In a subsequent study by Byberg [86BYB2], the preparation of BrO in the crystal state was examined. The EPR and x-irradiation of solid $KBrO_3$ is shown to produce complex defects of the composition [BrO, O_2]. The EPR spectra of $KBrO_3$(cr) recorded at 26 K after x-irradiation contained signals from at least six defects in spin-doublet and ground state. But the thermal formation of [BrO, O_2] in the photolyzed $KBrO_3$(cr) indicated that BrO_3^* produced [BrO, O_2] by reaction with a photoinduced precursor R, $BrO_3^* + R \rightarrow$[BrO, O_2]. (See Table 5.1.2.)

The conclusions to be drawn from the EPR studies are that the ground state is $^2\Pi_{3/2}$ (inverted doublet). For comparison, the laser magnetic resonance study of [81MCK] yielded rotational and spin orbit coupling constants. These values are included in Table 5.1.2.

Dissociation Energy Studies

There are two experimental spectroscopic studies which yield dissociation energy values: [47COL/GAY, 58DUR/RAM]. It is important to note that the excited state dissociates to Br($^2P_{3/2}$)+O($^1D_2$).

1. A linear Birge–Sponer extrapolation of the Coleman and Gaydon (1947) data gave 17800 cm^{-1} (2.21 eV or 50.9 kcal) for the dissociation energy of the ground state. Assuming that this extrapolation is high by perhaps as much as 20% [53GAY], Coleman and Gaydon recommended 14240 cm^{-1} (1.75 ± 0.3 eV or 40.7 kcal).
2. As stated by Durie and Ramsay [58DUR/RAM], the absorption spectrum of BrO was not observed to the dissociation energy limit. The limit was determined by extrapolating an equation representing the band heads and by a graphical Birge–Sponer technique. The limit was determined to be approximately 35200 cm^{-1}. Subtracting the $^1D_2 - ^3P_2$ excitation energy of the oxygen atom (15867.862 cm^{-1}), the dissociation energy is calculated to be 19332 ± 200 cm^{-1} (2.40 ± 0.02 eV or 55.3 kcal/mol). Durie and Ramsay reported the dissociation energy to be 19330 cm^{-1} whereas the actual calculation yields 19332 cm^{-1}.

Table 5.1.3 lists all studies which mention the dissociation energy of BrO. There are numerous articles which refer to dissociation studies, some of which simply extract earlier reported values or calculate them anew, and others which reassess data from the two experimental spectroscopic studies listed above.

TABLE 5.1.3. Dissociation energy of BrO ($D_0°$).

Source	eV	kcal/mol	kJ/mol	Comments
Experimental				
47COL/GAY		40.7	170	See discussion
58DUR/RAM		55.3	231	See discussion
Calculation				
77GLI		50.9	213	Used experimental ΔH_f values to calculate mean bond dissociation energies; the calculated D_1 value was derived from a ΔH_f value of [53BRE] but this latter value was not reported
88IGE/STO	1.32		127	SCF/CI calculations of the fourth row main group oxides (for the oxides K through Br the D_e values are consistently underestimated except for KO); dissociation energy value compared with a 2.45 eV value presumably from [79HUB/HER] (This is not what appears in these authors' book); bond length r_e=1.741 Å and vibrational frequency ω_e=726±10 cm^{-1} were also calculated
Comparisons				
77VOG/DRE				Used value extracted from [68GAY]
78DUN/DYK				Photoelectron spectroscopy study of ionization potential: quotes dissociation value of [58DUR/RAM]
81BOH/SEN				Mentioned dissociation energy but did not give a value
84SAU/TAT				Adopted value recommended by [79HUB/HER]
88TYK				Reported values extracted from existent sources; no new data
92GIL/POL				Photoelectron spectroscopic study; no new values given
Re-assignments				
50BRE/BRO				No direct values are given
50HER	2.2		212	Also refers to 1.75 eV as derived from [47COL/GAY]
53BRE				No value given but reference made to an earlier study [50BRO/BRE]
53GAY	1.8±0.5	42	176±48	Linear Birge–Spone extrapolation (L.B.X.) (ν, 0-7) 2.2 eV, but signs of negative curvature; analogy with ClO and IO favors high value; [47COL/GAY]
54COT	2.2 1.8±0.5		212 176±48	Values extracted from [50HER] and [53GAY] respectively; spectroscopic evidence is uncertain; Gaydon's upper limit, which agrees with [50HER] LBSX value, is more in accord with D_0(ClO), but even this seems low
58BRE		51	213	Value reported by Brewer with no explanation as to its origin
63SCH	1.8±0.5		176±48	Value extracted from [53GAY]
65GLU/MED		55.3±0.6	231±3	Values based primarily on the study of [58DUR/RAM]
66VED/GUR		55.3±0.6	231±3	Extrapolation of $A^2\Pi$ levels; assumed dissociation limit goes to Br($^2P_{3/2}$)+O(^{1}D); interpretation taken from Gurvich's early review (1962)
68GAY	2.40±0.02	55.2	231	L.B-S.$X^2\Pi$ 2.7 eV. Good G.B.-S.$A^2\Pi$, assuming limit is to O(^{1}D), 2.40±0.02. [58DUR/RAM]
68WAG/EVA		55.3±0.6	231±3	Results based solely on the work of [58DUR/RAM]
70DAR		55.2	231	Spectroscopy, adopted [58DUR/RAM] value;
		55.3±0.6	231±3	Extrapolation of $A^2\Pi$ [66VED/GUR];
		55.27	231	Extracted from[65WAG/EVA];
		55.3±0.1	231±1	Recommended by [70DAR]
79HUB/HER	2.39±0.01		230.6±1.0	Taken from near convergence of the absorption bands $A-X_1$; assumes dissociation of A into Br($^2P_{3/2}$)+O($^1D_2$)
82WAG/EVA		55.3±0.6	231±3	Results based solely on the work of [58DUR/RAM]
89GUR/VEY		55.28±0.6	231.3±3	Based on short extrapolation of the levels in the $A^2\Pi_i$ state; authors mention three kinetic studies which lead to less accurate values
94RUS/BER		55.3±0.6	231±3	Value given at 0 K; source of value unknown

Clyne and co-workers [77CLY/WAT, 77CLY/CUR] tabulated enthalpy of reaction for reactions involving BrO. The enthalpy of formation in these calculations was not specifically given but was said to have been taken from the best available information at the time (1976).

We adopt the interpretation of [79HUB/HER] for the dissociation energy of BrO. (See Table 5.1.3.)

5.2. BrO_2 (OBrO)

All references dealing with BrO_2 are listed in the following eight categories. This listing is somewhat arbitrary but is intended to give the reader a purview of the reported data. Of prime interest for this article are the spectroscopic and bond dissociation energy studies.

1. Formation/preparation/decomposition
   [37SCH/SCH], [38SCH/WIE], [39SCH/JAB], [39SCH/WIE], [40MUN/SPI], [59SCH/JOE], [62GUE/PAN], [71SHE/TUR], [74SOL/KEI], [80JAF/MAI], [83BUT/MOR], [90LEV/OGD]
2. Formation in crystal matrix or solution -
   [62BOY/GRA], [68BUX/DAI], [69AMI/CZA], [69BAR/GIL], [70AMI/TRE], [71OSL], [91SZA/WOJ]
3. BrO_2 as an intermediate -
   [85BEN/KRI], [85STE], [86BEN/KRI, [90SAS/HUI]
4. Reaction -
   [53PFL], [55PFL], [72FIE/KOR], [76HER/SCH], [78FOE/SCH], [80FOE/LAM], [80FOE/LAM2], [82FOE/LAM], [82FOE/LAM2], [82FIE/RAG], [83FIE/RAG], [83FOE/LAM], [85FOE/LAM], [86HUI/NET], [88NET/HUI], [89FOE/NOS], [91SZA/WOJ], [94HJE/ROS]
5. Enthalpy of formation/bond dissociation energy -
   [51PFL/SCH], [54COT], [66VED/GUR], [68WAG/EVA], [82WAG/EVA], [89STA], [95HUI/LAS]
6. Spectroscopy/structure -
   [73BYB/SPA], [73PAS/POT], [76PAS/PAV], [78TEV/WAL], [83BUT/MOR], [89BOW/BOY], [94RAT/JON], [95MAI/BOT], [95MUE/MIL]
7. EPR -
   [66CHA/BOY], [70COL/COS], [71BYB], [72RAO/SYM], [75BYB/LIN], [75DAL/LIN], [77SAS/RAO], [79CAR/SAH]
8. Review -
   [60GEO], [63SCH/BRA], [72BRI], [84BUR/LAW], [84JAC], [90JAC], [94JAC]

BrO_2 was first mentioned in the literature in 1937 [37SCH/SCH]. Schwarz *et al.* [37SCH/SCH], [38SCH/WIE], [39SCH/JAB], [39SCH/WIE] discussed the preparation of BrO_2.

Schwarz and Schmeisser [37SCH/SCH] studied the reaction of bromine with ozone which produced BrO_2 as a light yellow solid. This compound did not melt but decomposed spontaneously to the elements at approximately 0 °C.

Schwarz and Wiele [38SCH/WIE] studied the thermal decomposition of BrO_2. In addition to the formation of the elements, the authors also detected a white oxide which they presumed was Br_2O_7 or Br_2O_6 and a dark-brown oxide, Br_2O. Schwarz and Wiele [39SCH/WIE] continued their study of the thermal decomposition of BrO_2. Their study showed that BrO_2 is completely stable at −40 °C, but that decomposition can be detected manometrically as the temperature is increased. Br_2O is stable at −40 °C. Again Br_2O_7 was suggested as one of the decomposition products of BrO_2.

Mungen and Spinks [40MUN/SPI], in examining the decomposition of ozone in the presence of bromine, detected the formation of a number of bromine oxides, including BrO_2.

The remaining studies of the formation of BrO_2 are based on variations of these above-mentioned procedures. Solomon and Keith [74SOL/KEI] made several attempts to prepare BrO_2, including the glow-discharge method of [37SCH/SCH]. The techniques used produced bromine oxides of variable composition including BrO_2, BrO_3 and $BrO_{2.71}$ (very close to Br_3O_8). Much of this work was reviewed by [63SCH/BRA] and [72BRI], as well as in the Gmelin series mentioned in the Introduction.

There are numerous EPR studies. None of these studies provide any information as to the structure of BrO_2.

Chase and Boyd [66CHA/BOY]: radiolysis of crystalline alkaline earth bromates by cobalt-60 γ-ray, suggested that BrO_2 was produced and stabilized in the crystal lattice.

Collins *et al.* [70COL/COS]: irradiated zinc bromate, experimental evidence suggested the formation of a paramagnetic center in the crystal which was attributed to BrO_2.

Byberg [71BYB]: x-ray irradiated $KBrO_4$ crystals at 10 or 26 K, spectra interpreted to indicate the existence of BrO_4 which then, thermally dissociated to BrO_2.

Rao and Symons [72RAO/SYM]: x-ray irradiated crystalline bromates, EPR spectra of BrO_2 in part based on seeing the effects of two isotopes ^{79}Br and ^{81}Br, both having I=3/2, proposed a formation route for BrO_2, results stated to differ from the Collins *et al.* [70COL/COS] data.

Byberg and Linderberg [75BYB/LIN]: x-ray irradiated perbromate crystals, suggested the formation of a weakly bound complex of the composition (BrO_2•O_2), no evidence that BrO_2 existed as a separate entity.

Dalgard and Linderberg [75DAL/LIN]: molecular theory calculational model for the EPR study of quadrupole and hyperfine interaction tensors of BrO_2, BrO_4, and BrO_6; x-ray irradiation of $KBrO_4$ led to the formation of the $(BrO_2 \cdot O_2)$ complex.

Sastry and Rao [77SAS/RAO]: EPR identification of the formation of BrO_2 in a γ-irradiated cadmium bromate dihydrate.

Carlier *et al.* [79CAR//SAH]: EPR of BrO_2, spectrum was similar to that observed by [72RAO/SYM].

There are a number of spectroscopic studies which provide vibrational frequencies and structural information. These are summarized in Table 6.

Byberg *et al.* [73BYB/SPA], stated that in 1973, no structural information was available for BrO_2. Modified extended Huckel theory was used to calculate nuclear quadrupole coupling constants. Comparing calculated values with observed values helped confirm the geometry of BrO_2: C_{2v} symmetry with a bond length of 1.625 Å and a bond angle of 117.6°. This geometry was that of ClO_2 with an adjustment for the presumed differences in BrO and ClO. The nuclear quadrupole coupling constants are not as sensitive to the bond angle as they are to the bond distances. The authors stated that any reasonable changes will not improve interpretation.

Pascal *et al.* [73PAS/POT, 76PAS/PAV] indicated that BrO_2 exists as Br_2O_4 with a Br–Br bond. The authors ob-

Table 6. Polyatomic bromine oxide species: Structure and vibrational frequencies.

		Bond Distance r(Å)			Vibrational Frequencies				
Source	Structure	Br–O	O–O	Br–Br	ν_1	ν_2	ν_3		Comments
BrO_2 (OBrO)									
73BYB/SPA	C_{2v}, 117.6°	1.625							Modified extended Huckel theory used to calculate nuclear quadrupole coupling constants; calculated values for structure
73PAS/POT									Raman spectra in crystalline form indicated that BrO_2 exists as Br_2O_4 with a Br–Br bond
78TEV/WAL	*110±2°						852		Infrared spectra of the isolated radical in an Ar matrix; *apex angle determined on identification of ν_3 asymmetric stretch; ^{18}O isotopic enrichment experiments used to identify molecules
83BUT/MOR	C_{2v}, 118°	2.9							Mass spectrometry; discharge-flow system; reaction of $O+Br_2$; assumed structure (in analogy with OClO) and calculated rotational constants
84JAC, 90JAC 94JAC							852		Review recommended ν_3 value from Ar matrix study of 78TEV/WAL
89BOW/BOY	C_{2v}, 117.6°	1.625							SCF multiple scattering X-α calculations of the bonding and nuclear quadrupole coupling in BrO_2; adopted geometry of [73BYB/SPA]
95MAI/BOT	C_{2v}				$O^{81}BrO$ 791–797 $O^{79}BrO$ 794–799		$O^{81}BrO$ 842–844 $O^{79}BrO$ 845–847		IR absorption; matrix isolation at 12 K
95MUE/MIL	C_{2v}, 114.4°	1.649							Microwave study, preliminary analysis also supportive of ν_2 approximately equal to 300 cm^{-1}
BrOO									
70CLY/CRU									Electronic absorption spectrophotometry in a discharge-flow system of BrO; formation of BrOO in $BrO+BrO\text{-}k_2 \rightarrow Br+BrOO \rightarrow Br+O_2$ disproportionation reaction
78TEV/SMA					1487				Infrared spectra of the isolated radical in an argon matrix
79MIC/PAY					872	100			BEBO calculations, stated to be indeterminate for the bending frequency; value suggested for ν_2 is consistent with the authors' kinetic data in the region 200–360 K
83BUT/MOR	C_s, 120°	2	1.5						Mass spectrometry; discharge-flow system; assumed structure (in analogy with Br–O–O–Br structure suggested by 70CLY/CRU) and calculated rotational constants
84JAC, 90JAC					1487				Review recommended ν_1 value from Ar matrix study of 78TEV/SMA
95MAI/BOT	C_s				$Br^{16}O_2$ 1475.5–1484.0 $Br^{16}O^{18}O$ 1430–1432.1				IR absorption; matrix isolation at 12 K; the vibrational frequency assigned to $Br^{16}O^{18}O$ is in fact a mixture of $Br^{16}O^{18}O$ and $Br^{18}O^{16}O$
BrO_3					ν_1	ν_2	ν_3	ν_4	
56VEN/SUN	C_{3v}, 89°	1.68			442	800	35 0	828	References observed Raman frequencies, however it appears adopted frequencies are approximations derived from the ion; bond distance calculated by Badger's rule; calculation of force constants
63VEN/RAJ	C_{3v}, 89°				442 439	800 806	35 0 35 0	828 815	Urey-Bradley potential force field; although the authors refer to observed vibrational frequencies there is no specific reference to these observations; observed and calculated frequencies given respectively; calculation of force constants
64RAO/SYM	C_{3v}								Vibrational mean square amplitude theory; two totally symmetric A_1 and identifies six vibrations, modes; no data provided; two doubly degenerate E mean square amplitudes calculated

Table 6. (Continued.)

Source	Structure	Bond Distance r(Å) Br–O	O–O	Br–Br	Vibrational Frequencies ν_1	ν_2	ν_3	ν_4	Comments
70BEG/SUB	C_{3v}, 114°								ESR; formation of BrO_3 from γ-radiolysis of potassium bromate at 77 K; structure identified; magnetic parameters given
72RAO	C_{3v}								Centrifugal distortion constants; classifies the six vibrations as two totally symmetric A_1 and two doubly degenerate E modes but no values were given
74BYB/KIR	*C_s								*ESR crystal study of paramagnetic defects in x-irradiated $KBrO_3$ suggests that the species is BrO_3^- rather than BrO_3; KNO_3:$KBrO_3$ exhibits the BrO_3 species with a cylindrical spin Hamiltonian analogous to that of ClO_3; calculated bond distance based on ClO_3
77LEE/BEN		1.66							EXAFS spectra; prediction of bond length
78THI/MOH	C_{3v}, 89°	1.79			800	442	82 8	350	Group theoretical method; vibrational frequencies calculated for ν_1 and ν_2 are reversed, the same is true for ν_3 and ν_4; force constants are calculated
85BYB	C_{3v}, 112°	1.57							Values proposed earlier by 74BYB/KIR to account for the spin Hamiltonian of BrO_3 in KNO_3:$KBrO_3$;
	105.5°	1.56	1.72	1.64					ESR spectra in $KClO_4$:$KBrO_3$; author proposes a new asymmetric structure for BrO_3 with bond distances for ($Br–O_3'$), ($Br–O_2$) and ($Br–O_3$), respectively
86UMA/RAM	C_{3v}								ESR γ-irradiation of crystal $KBrO_3$ and $Sr(BrO_3)_2 \cdot H_2O$; MO calculations using the CNDO/2 method; NQR experimental values
BrOBr					ν_1	ν_2	ν_3		
54ANT/DOJ									UV absorption spectra of Br_2O in CCl_4; strong absorption band at 2800 Å (35714 cm^{-1})
68CAM/JON	C_{2v}, 113°				504	197	587		IR spectra of the crystal Br_2O and ^{18}O-enriched Br_2O;spectra most satisfactorily explained in terms of C_{2v} symmetry; comparisons with F_2O and Cl_2O were used in explaining data; force constants were calculated
72BRI	113°				504	197	583		Review based crystal study by 68CAM/JON; calculation of force constants
77PAS/PAV					504	197	590		Raman analysis (species observed in a matrix at 50 °C) corroborates previous IR studies; assumed the formation of Br_2O from decomposition of Br_2O_3
78PAS					506		592		IR spectra of the crystal Br_2O
78TEV/WAL	87°				526.1		504		IR spectra of the isolated radical in an argon matrix; states that the values assigned by 68CAM/JON for ν_1 and ν_3 are reversed and questioned the ν_3 reasonableness of the bond angle; ^{18}O isotopic enrichment experiments used
84BOL/BAL	Linear				250	245	800		Extended x-ray absorption spectra of thermally excited vibrations; frequencies were used to calculate force constants; no preferred structure was recommended; estimates of the vibrational frequencies as a function of bond angles
84EPI/LAR									MOVB theory; no data provided
84JAC, 90JAC, 94JAC					526.1		623.4		Review recommended ν_1 and ν_3 values from Ar matrix studies by 78TEV/WAL and 87ALL/POL
87ALL/POL	*113° or 87°				526.1		623.4		IR spectra of matrix isolated radical; *bond angle depend on relative assignment of ν_1 and ν_3
90LEV/OGD	C_{2v}, 112±2°	1.85		3.07	508		595		IR and UV-VIS spectroscopy and bromine k-edge EXAFS of the solid radical; consistent with the results of 68CAM/JON and 78PAS

Table 6. (Continued.)

Source	Structure	Bond Distance r(Å) Br–O	O–O	Br–Br	Vibrational Frequencies ν_1	ν_2	ν_3	Comments
92NOV	C_{2v}, 115.69°	1.80902						*Ab initio* calculations and an extended basis set; comparable with the results of 90LEV/OGD
95LEE	C_{2v}, 112.9°	1.865			512	180	613	*Ab initio* calculations—CCSD(T)
95MUE/COH	C_{2v}, 112.24°	1.8429			···	180	···	Microwave spectra for three isotopomers
BrBrO								
73DIX/PAR	150°							Reaction complex O–Br–Br; plausible triplet ground state at α=180°, however, an improved approximation might change α to 150°
73PAR/HER								Cross-beam experiments involving collision of O atoms with Br molecules; predicts an O–Br–Br nonlinear complex with a triplet ground state
78TEV/WAL					804	<200	236	Infrared spectra of the Ar–Br_2–O_3 matrix isolated radical; the Br–Br bending mode are based on comparison with the Cl–Cl stretch and ClClO bending mode of ClClO
80VEL/DUR								Cross-beam scattering; stated reactive results are consistent with the long-lived triplet of the OBrBr complex as suggested by 78TEV/WAL and 73PAR/HER
82FER/SMI	$^3A''$							Reactive scattering of O atoms with Br_2; proposed existence of a shortlived OBrBr collision complex with a bent configuration and with a modest E_0 of approximately 110 kJ/mol; supports the conclusion of 73PAR/HER
84JAC, 90JAC, 94JAC 87LOE/AND					804		236	Review recommended ν_1 and ν_3 from Ar matrix study by 78TEV/WAL Frontier orbital theory and Lewis electronic structure theory; proposed existence of a long-lived intermediate of a cyclic BrBrO structure
95LEE	113°	1.690	2.510		793	215	153	*Ab initio* calculations—CCSD(T)
Br_2O_2		Br–O	O–O	Br–O				
68EDW/GRE								Rate law stoichiometry; classified as $BrBrO_2$
70CLY/CRU	120°	1.64	1.5	2.0				Electronic absorption spectrophotometry in a discharge-flow system of BrO; transition-state theory; a symmetrical planar bent chain triplet species with a structure (BrOOBr) was assumed; estimated in comparison with ClOOCl
78TEV/WAL								IR argon matrix spectroscopy; photolysis; weak bands appeared at 831.7, 830.2, and 760.3 cm^{-1}; identified the most likely structure of Br_2O_2 as an open chain when the Br–Br bond remains intact (OBr–BrO), and a (BrOBrO) structure formed by the insertion of an oxygen atom into the weakened Br–Br bond
84EPI/LAR								MOVB theory; reference to this species in table but no data provided
Br_2O_3								
74PAS/PAV								Prepared from the thermal decomposition of Br_2O_4; Raman absorption and IR spectra; the vibrational spectrum of Br_2O_3 shows the presence of a BrOBr bond but it was not possible to distinguish between the two forms (OBrOBrO and $BrOBrO_2$)
76PAS/PAV	C_s							Raman spectra; suggested a (OBrOBrO) structure for Br_2O_3; some vibrational frequencies have been assigned to specific vibrational modes
77PAS/PAV								Raman spectra; suggested a symmetric structure (OBrOBrO); some frequencies have been assigned to specific vibrational modes
87ALL/POL							973.1–1029.6	IR spectra of a crystalline Br_2O_3 in argon matrix; not able to determine which structure ($BrOBrO_2$ or OBrOBrO) existed; the symmetrical structure was adopted based on comparison of Raman spectra of Br_2O_3 and Br_2O_4

Table 6. (Continued.)

Source	Structure	Bond Distance r(Å) Br–O	O–O	Br–O	Vibrational Frequencies ν_1	ν_2	ν_3	Comments
93STI								Proposed anionic structure of $Br^{+}BrO_3^{-}$ for Br_2O_3
Br_2O_4								
73PAS/POT	C_{2v} or C_2				861–882	205	910–919	Raman spectra at −180 °C;
(O_2BrBrO_2)								Br_2O_4 is classified as having a dimeric structure ($O_2Br–BrO_2$) with a Br–Br bond
74PAS/PAV (O_2BrBrO_2) 76PAS/PAV ($O_2BrOBrO$)								Raman spectra; suggested structure to be (O_2BrBrO_2) Raman spectra; suggested structure of the two isomers of Br_2O_4 to be (O_2BrBrO_2) and ($O_2BrOBrO$); some vibrational frequencies have been assigned to specific vibrational modes of the two symmetric and asymmetric isomers
77PAS/PAV ($O_2BrOBrO$)	C_{2v} or C_2							Raman spectra; suggested structures (O_2BrBrO_2) and ($O_2BrOBrO$) for the two isomers of Br_2O_4; some frequencies have been assigned to specific modes of the symmetric and asymmetric isomers
92GIL/LEV ($BrBrO_4$)	110±3°							Spectroscopic and EXAFS data on solid compound; interatomic distance given
Br_2O_5								
77PAS/PAV								Based on the Raman spectra and structure of Br_2O_3 and Br_2O_4, an I_2O_5 analogous polymer structure is proposed for Br_2O_5

served the Raman spectra of the crystalline bromine dioxide at −180 °C in a sealed tube *in vacuo*. There is no structural or vibrational information provided directly for BrO_2(g), although tentative assignments had been made for the crystalline dimer.

Tevault *et al.* [78TEV/WAL] studied the reaction of atomic and molecular bromine with atomic and molecular oxygen in argon matrices (photolysis of bromine and ozone containing matrices). Several bromine oxygen compounds were stated to have been formed and identified by infrared spectroscopy — BrO, OBrO, BrBrO, BrOBr, and $(BrO)_2$. The apex angle of BrO_2 was calculated to be 110±2° based on three facts:

1. The proper identification of the symmetric stretching frequency ν_3 to be 852 cm^{-1},
2. Observed frequency shifts with the use of $^{18}O_3$, and
3. Splitting due to the naturally occurring bromine isotopes (^{79}Br and ^{81}Br).

Bowmaker and Boyd [89BOW/BOY] assumed the BrO_2 geometry as suggested by [73BYB/SPA] in performing an SCF-Xα study of the bonding and nuclear quadrupole coupling in BrO_2. Butkovskaya *et al.* [83BUT/MOR], in their kinetic studies, proposed a C_{2v} structure with a bond angle of 118° and a bond distance of 2.9 Å by analogy with OClO. This series was detected by modulated beam mass spectrometry. Magnetic and electric field beam focusing revealed that OBrO is a paramagnetic molecule with a C_{2v} symmetry.

Jacox [84JAC], [90JAC], [94JAC], in her reviews, recommended a ν_3=852 cm^{-1} asymmetric stretch value, based on the work of [78TEV/WAL].

Rattigan *et al.* [94RAT/JON] observed a visible absorption spectrum arising from OBrO in the bromine sensitized decomposition of ozone. The authors provided spectral evidence for the $A^2A_2 \leftarrow X^2B_1$ electronic transition. They reported $\nu_{0,0,0}$= 16178 cm^{-1} and approximate vibrational frequencies for the excited state (ν_1=600 cm^{-1} and ν_2=200 cm^{-1}).

Preliminary results of a microwave study of OBrO(g) by Mueller *et al.* [95MUE/MIL] suggested a bent structure, r(Br–O)=1.649 Å and <(OBrO)=114.4°. They also observed the ν_2 and $2\nu_2$ states, but the relative intensities were not measured. Results are consistent with a ν_2 value of approximately 300 cm^{-1}.

Maier and Bothur [95MAI/BOT] studied the flash photolysis of a gas mixture containing bromine, oxygen and argon. BrO_2 was formed by the matrix irradiation of BrOO. The IR absorption of two isomers ($O^{81}BrO$ and $O^{79}BrO$) was observed at three different concentration ratios of $Br_2/O_2/Ar$ and values for ν_1 and ν_3 were assigned.

Pflugmacher *et al.* [51PFL/SCH] experimentally measured the enthalpy of formation of BrO_2 (cr). The value reported was −12.5±0.7 kcal which, in fact, refers to the decomposition heat. The formation reaction is the reverse of what was measured. Wagman *et al.* [68WAG/EVA], [82WAG/EVA], in their reviews, assumed that the measured value referred to the energy of the reaction (not the enthalpy) and corrected the value for a Δ(pv) term, adjusted the value from −45 °C to 25 °C, thus resulting in a value of 11.6 kcal/mol for the enthalpy of formation of BrO_2(cr). Glushko and Medvedev (1965) adopted 12.5 kcal/mol as the enthalpy of formation.

Cottrell [54COT] reported D(O–BrO) ⩾ 70±10 kcal/mol. (This converts to $\Delta_f H$=87.3 kJ/mol.) This value was based on the enthalpy of formation of BrO_2(cr) reported by [51PFL/SCH] and D_0(BrO)=2.25 eV or 50 kcal/mol. Cottrell expressed doubt as to the validity of this value based on comparison with ClO_2. The enthalpy of dissociation reported by [66VED/GUR] is $\Delta H(298) \geq 70$ kcal/mol for the reaction $BrO_2 \rightarrow BrO + O$. This is an estimated value based on the work by Cottrell (1954). In contrast Huie [95HUI/LAS] has estimated the ethalpy of formation of OBrO(g) in the following manner. According to Stanbury [89STAN], the enthalpy of formation of OBrO in the gas phase can be estimated from the value of $\Delta G^0 = 144$ kJ mol^{-1} in the aqueous phase by comparison with the gas and aqueous phase values for OClO. Taking $\Delta G^0 = 120.5$ kJ mol^{-1} for OClO(g) and $\Delta G^0 = 117.6$ kJ mol^{-1} for OClO(aq) [Wagman, 1968] and assuming the same ratio applies for OBrO, we obtain $\Delta G^0 = 148.0$ kJ mol^{-1} for OBrO(g) and $\Delta_f H^0 = 130$ kJ mol^{-1}.

5.3. BrO_2 (BrOO)

All references dealing with BrOO are listed in the following four categories. This listing is somewhat arbitrary but is intended to give the reader a purview of the data. The structure and vibrational frequencies of this molecule are summarized in Table 6.

1. Formation as an intermediate in kinetic schemes - [69IP/BUR], [70BLA/BRO], [70CLY/CRU], [77CLY/CUR], [80JAF/MAI], [81SAN/WAT], [83BUT/MOR], [86SAN], [88TOO/BRU], [93MAU/WAH]
2. Reviews - [77CLY/CUR], [84BUR/LAW], [84JAC], [90JAC], [94JAC]
3. Spectroscopy/structure - [70CLY/CRU], [78TEV/SMA], [79MIC/PAY], [83BUT/MOR], [95MAI/BOT]
4. Enthalpy of formation/ dissociation energy - [69IP/BUR], [70BLA/BRO], [70CLY/CRU], [81SAN/WAT], [83BUT/MOR], [88TOO/BRU], [95HUI/LAS]

Butkovskaya *et al.* [83BUT/MOR], in their kinetic studies, proposed a C_s structure with a bond angle Br–O–O–120° and bond distances of r(Br–O)=2 Å and r(O–O)=1.5 Å. [83BUT/MOR] referred to the [70CLY/CRU] study to aid in estimating a structure for BrOO.

Michael and Payne [79MIC/PAY] discussed a calculational approach (BEBO) in which they determined $\nu_1 = 872$ cm^{-1}. Although this method was stated to be indeterminate for the bending frequency, the authors did suggest that a value of $\nu_2 = 100$ cm^{-1} was consistent with their kinetic data in the region of 200–360 K.

Jacox [84JAC], [90JAC], [94JAC] reviewed the spectroscopic properties of BrOO; the sole reference being the spectroscopic work by Tevault and Smardzewski [78TEV/SMA] on the infrared spectrum of the Ar matrix isolated radical. The measurement provided an O–O stretching frequency of 1487 cm^{-1}. There are no gas phase studies which characterize this molecule.

Maier and Bothur [95MAI/BOT] studied the flash photolysis of a gas mixture containing bromine, oxygen and argon. BrOO was produced by this process. The IR absorption of three isomers ($Br^{16}O^{18}O$, $Br^{18}O^{16}O$, and $Br^{16}O_2$) was observed and values for ν_1 were assigned.

A number of authors have cited an enthalpy of formation [81SAN/WAT], [88TOO/BRU] or a bond dissociation energy [70CLY/CRU], [83BUT/MOR], [95HUI/LAS] for BrOO. However, all of these studies are based on the work by Blake *et al.* [70BLA/BRO].

Ip and Burns [69IP/BUR] determined the recombination rate constants of bromine atoms in the presence of six different third bodies (helium, neon, argon, krypton, oxygen and nitrogen) over the temperature range of 300 and 1273 K. The authors refer to two earlier studies: Rabinowitch and Wood [36RAB/WOO] and Strong *et al.* [57STR/CHI]. Based on these data, Blake *et al.* [70BLA/BRO] calculated interaction potentials between atomic bromine, oxygen and an inert third body (such as a rare gas). A value was given for $Br-O_2$. BrOO was thought to be unstable with a bond energy (Br–OO) of approximately 1 kcal/mol which translated to an enthalpy of formation of 108 kJ/mol.

5.4. BrO_3

The articles pertaining to BrO_3 may be classified as follows.

1. Formation/preparation - [28LEW/SCH], [29LEW/SCH], [29LEW/SCH2], [30LEW/SCH], [38CSH/WIE], [39SCH/WIE], [40MUN/SPI], [53PFL], [55PFL], [55PFL/RAB], [58ARV/AYM], [59ARV/AYM], [59PFL], [59SCH], [60BRI/MAT], [62GUE/PAN], [74SOL/KEI], [82MUK/KHI]
2. Radiolysis - [60MAT/DOR], [62BOY/GRA], [70AMI/TRE], [70BEG/SUB], [71SER/ZAK]
3. Spectroscopy/structure - [56VEN/SUN], [63VEN/RAJ], [64RAO/SAN], [72RAO], [77LEE/BEN], [78THI/MOH], [84SAS/RAO], [85BYB], [86UMA/RAM]
4. EPR - [70BEG/SUB], [71SER/ZAK], [72RAO/SYM], [74BYB/KIR], [85BYB]
5. Review - [34BRA], [60GEO], [63SCH/BRA], [80KOL], [84JAC]
6. Enthalpy of formation - [48FAR/KLE]

Early work refers to the formation in the condensed phase of the trioxide (or its dimer, the hexoxide).

There is no confirmatory information as to the proper characterization. There are many articles dealing with the formation or reaction of BrO_3. Pflugmacher *et al.* [55PFL/RAB] studied the reaction of bromine with excess O_2 in a glow discharge at 0 °C. BrO_3 was claimed to be the product. Although the ratio was 1:3, it is not clear that the product was BrO_3. The compound formed was claimed to decompose above −70 °C. Also, the method of Lewis and Schumacher [29LEW/SCH], in which the reaction of bromine with ozone was claimed to produce Br_3O_8, was reproduced here with a larger excess of ozone and yielded BrO_3 (in the condensed phase).

Arvia *et al.* [59ARV/AYM] studied the thermal reaction between bromine and ozone. Under different conditions, they observed Br_2O_5 and Br_3O_8. The authors specifically stated that BrO_3 or Br_2O_6 was not observed, contrary to the result of Pflugmacher. Pflugmacher [59PFL] and Schumacher [59SCH] responded to this article and further discussed possible interpretations of the results.

Solomon and Keith [74SOL/KEI] made several attempts to prepare BrO_2, including the glow-discharge method of [37SCH/SCH]. The techniques used produced bromine oxides of variable composition including BrO_2, BrO_3, and $BrO_{2.71}$ (very close to Br_3O_8).

EPR studies often provide information as to the structure of the molecule and the nature of the electronic ground state. In the case of BrO_3, the EPR studies were consistent with a C_{3v} symmetry but there was no definitive evidence to confirm this.

BrO_3 was produced by the γ-radiolysis of $KBrO_3$ at 77 K [70BEG/SUB]. From the EPR measurements of BrO_3 and an assumed C_{3v} symmetry, they calculated the bond angle to be 114°. The structure was distorted in the crystalline environment. The authors stated that the radical must be distorted from C_{3v} symmetry presumably because of an asymmetric environment of the potassium ions around the oxygen atoms of BrO_3. Similar results were reported in 1985 by Byberg [85BYB], in which the author reported that the BrO_3 radical had C_{3v} symmetry but some distortion might occur due to the nature of the host crystal. He discussed a bond angle of 112° and a bond length of 1.57 Å. The other studies provide no additional information.

The spectroscopic articles for the gas phase radical involved force field calculations of pyramidal XY_3 type molecules [56VEN/SUN, 63VEN/RAJ, 64RAO/SAN, 72RAO, 78THI/MOH]. Contrary to the implications of these five articles, there was no observed structural information nor was there any observed vibrational information. Upon examination of the earlier literature cited by these authors, vibrational frequency information was found for BrO_3^- in a crystalline environment. Two of the four vibrational frequencies matched exactly with those reported for BrO_3^-. These articles have assumed a pyramidal structure with an O–Br–O angle of 89° (the same angle was used for the chlorine, bromine, and iodine trioxides): a bond distance Br–O of 1.68 Å (from Badger's rule), and vibrational frequencies (in cm^{-1}) of ν_1=442 [A_1], ν_2=800 [A_2], ν_3=350 [E], and ν_4=828 [E].

Two additional studies provide insight into the structure of BrO_3. Electric field gradients at the halogen site in XO_3 and XO_3^{2-} radicals (X=Cl, Br), formed by the γ-irradiation of single crystals of $NaClO_3$, $KClO_3$, $KBrO_3$ and $Sr(BrO_3)_2 \cdot H_2O$ have been evaluated by MO calculations using the CNDO/2 method. The symmetry of the XO_3 radicals was assumed to be that of XO_3^- ions which have C_{3v} symmetry [86UMA/RAM]. Lee and Beni [77LEE/BEN], in their calculation of atomic phase shifts (as applied to extended x-ray absorption and fine structure in molecules and crystals) predicted a Br–O bond length of 1.66 Å in solution. No other information of BrO_3 was provided.

There is no reported information as to the experimental determination of the enthalpy of formation of this radical. There is a calculated value reported by [48FAR/KLE] of +23 kcal/mol. Although the authors, Farkas and Klein, stated that they calculated the enthalpy of formation of BrO_3 the formula given was BrO_3^-.

5.5. BrO_4

It is important to note that this oxide has not been isolated. There is no thermodynamic information and no spectroscopic information.

BrO_4 has been proposed to be formed:

(1) As a weak adduct, $BrO \cdot O_3$, in the disproportionation of BrO [90TUR/BIR]
(2) In the ^{60}Co γ-irradiation of an acidic aqueous glass containing perbromate ions [75GIN/SYM]
(3) In the X-irradiation of $KBrO_4$ crystals [71BYB]
(4) As a complex ($BrO_2 \cdot O_2$) during the X-irradiation of $KBrO_4$ (calculational model and EPR study) [75DAL/LIN]
(5) By the X-irradiation of $KClO_4$ single crystals doped with $KBrO_4$ [85BJE/BYB]
(6) During the X-irradiation of $KBrO_4$ single crystals in which a weakly bound complex ($BrO_2 \cdot 2O_2$) was formed which decayed to BrO_4 [75BYB/LIN].

5.6. Br_2O (BrOBr)

All references dealing with Br_2O are listed in the following six categories. Of prime interest are the spectroscopic studies and the enthalpy of formation calculation. The structure and vibrational frequencies of this molecule are summarized in Table 6. Br_2O has been experimentally studied in condensed media and in the gas phase.

1. Preparation/decomposition -
   [30ZIN/RIE], [31LEW/FEI], [35BRE/SCH], [36BRE/SCH], [38SCH/WIE], [39SCH/WIE], [40MUN/SPI], [61GUE/GOU], [62GUE/PAN]
2. Review -
   [34BRA], [60GEO], [63SCH/BRA], [72BRI], [84BUR/LAW], [84JAC], [90JAC], [94JAC]
3. Reaction -
   [47KLA/BOL], [53KAN], [69JEN/ZIE], [72BUN], [72BUB2], [76ODY/NEC], [79MIT], [89FLE/SWA], [87SWA/FLE], [94DNE/ELI], [95HEU/HAN]
4. Spectroscopy/structure -
   (In solution) -[54ANB/DOS]
   (In crystal) - [68CAM/JON], [77PAS/PAV], [90LEV/OGD]
   (In matrix) - [78TEV/WAL], [87ALL/POL], [90LEV/OGD]

(In gas) - [73PAR/HER], [84BOL/BAL], [84EPI/LAR], [92NOV], [95LEE], [95MUE/COH], [95ORL/BUR]

6. Enthalpy of formation - [92NOV], [95LEE], [95ORL/BUR], [95THO/MON]
5. Physical properties (viscosity, thermal conductivity) - [62SVE]
6. Misclassified (should be BrO) - [66CAR/LEV]

The earliest studies dealing with the preparation of Br_2O are based on work by [30ZIN/RIE], [31LEW/FEI], and [35BRE/SCH].

In a review article, Brady [34BRA] stated that Zintl and Rienacker [30ZIN/RIE] obtained small quantities of a volatile oxide, perhaps Br_2O, by two methods; (1) by passing bromine vapor over a specially prepared HgO at 50–60 °C, and (2) by mixing bromine vapor with ozone under reduced pressure at 0 °C. A subsequent study by Brenschede and Schumacher [35BRE/SCH] examined the reaction between HgO and bromine in a carbon tetrachloride solution. The method of preparation is given, as well as the self decomposition and the reaction with carbon tetrachloride in light [the same reaction occurred in dark in a few days]. The decomposition in light was presumed to be $Br_2O \rightarrow Br_2 + 1/2O_2$ and $Br_2O + CCl_4 \rightarrow COCl_2 + Br_2 + Cl_2$. A subsequent study by the same authors [36BRE/SCH] examined the same formation reaction. In addition, they studied the extinction curve of Br_2O dissolved in CCl_4 and the thermal and photochemical decomposition.

Schwarz and Wiele [38SCH/WIE] studied the thermal decomposition of BrO_2. In addition to the formation of the elements, the authors also detected a white oxide which they presumed was Br_2O_7 or Br_2O_6 and a dark-brown oxide, Br_2O. Schwarz and Wiele [39SCH/WIE] continued their study of the thermal decomposition of BrO_2. Their study showed that BrO_2 is completely stable at −40 °C, but that decomposition can be detected manometrically. BrO_2 sublimes with extensive decomposition, melting in dry air at approximately −17.5 °C. Br_2O is stable at 40 °C. Again Br_2O_7 was suggested as one of the decomposition products of BrO_2.

Lewis and Feitknecht [31LEW/FEI], in examining the decomposition of ozone in the presence of bromine, detected the formation of a number of oxides, but not Br_2O. The specific oxide formed was not identified. The remaining studies dealing with the formation of Br_2O are based on variations of these procedures. All studies involving the formation, preparation and decomposition of Br_2O are reviewed by [34BRA], [63SCH/BRA] and [72BRI], as well as in the Gmelin series discussed in the Introduction.

Anthar and Dostrovsky [54ANT/DOS] measured the ultraviolet absorption spectra of Br_2O in CCl_4. A strong absorption band was observed at 2800 Å (35714 cm^{-1}).

Parrish and Herschbach [73PAR/HER] observed, in their cross beam experiments, that the reaction of $O(^3P)$ with $Br_2(^1\Sigma_g^-)$ yielded $BrO(^2\Pi) + Br(^2P)$. The authors stated that this reaction occurred "via a persistent collision complex with large reaction yield and no activation energy, but the known, stable Br_2O molecule does not correlate with the reactants."

The IR spectra of the solid was most satisfactorily explained [68CAM/JON] in terms of a bent triatomic molecule with C_{2v} symmetry and a $\nu_1 = 504$ cm^{-1}, $\nu_2 = 197$ cm^{-1}, and $\nu_3 = 587$ cm^{-1}. The assumed bond angle was 113°.

Pascal *et al.* [77PAS/PAV] assumed that Br_2O was formed from the decomposition of Br_2O_3. The authors observed the symmetric stretch of Br_2O to be 504 cm^{-1}, the asymmetric stretch, 590 cm^{-1}, and assumed the bend to be 197 cm^{-1}. The Raman analysis of Br_2O corroborated the previous infrared work by Campbell *et al.* In a later study, Pascal [78PAS] reported $\nu_1 = 506$ cm^{-1} and $\nu_3 = 592$ cm^{-1} values.

The results of Tevault *et al.* [78TEV/WAL] are in contrast to those observed by Campbell *et al.* [68CAM/JON]. It appears that these authors assigned ν_1 a value of 526.1 cm^{-1} and they implied that the assignments of ν_1 and ν_3 by [68CAM/JON] are reversed. Using Tevault's value of ν_3, a minimum value of 87° was calculated for the bond angle.

Bolander and Baldeschwieler [84BOL/BAL] examined the dependence of the extended x-ray absorption fine structure, amplitude, and phase on thermally excited vibrations. The model system the authors studied was Br_2O. They assumed the symmetric stretch and bend occurred at 250 and 245 cm^{-1} in the linear structure, while the asymmetric stretch occurred at 800 cm^{-1}. These assumed frequencies were used to calculate force constants which were then assumed to be independent of the geometry of the molecule. No experimental data were referred to and no preferred structure was recommended. This article provided estimates of the vibrational frequencies as a function of bond angles.

Epiotis *et al.* [84EPI/LAR], using a MOVB theory, referred to Br_2O in a table but provided no information.

Allen *et al.* [87ALL/POL] studied the IR spectra of matrix isolated Br_2O and assigned ν_3 to be 623.4 cm^{-1} and ν_1 to be 526.1 cm^{-1}. The authors referred to a bond angle of 113° or 87° based on the ν_3 isotopic shift information.

Levason *et al.* [90LEV/OGD] studied Br_2O (cr) by infrared and UV-VIS spectroscopy and bromine K-edge extended x-ray absorption fine structure (EXFAS). This is the first definitive structural analysis study for the bromine oxides (Br_2O_3 was definitively analyzed at a later date by others). The authors' results are consistent with the IR spectra of Br_2O obtained by Campbell *et al.* [68CAM/JON], the ^{18}O results which demonstrated that solid Br_2O is molecular, and with experiments by Pascal [78PAS] who reported $\nu_1 = 506$ cm^{-1} and $\nu_3 = 592$ cm^{-1}. The data were consistent with C_{2v} symmetry and a bond angle (Br–O–Br) of 112±2° and bond distance r(Br–O)=1.85 Å.

With the aid of *ab initio* calculations and an extended basis set, Novak [92NOV] calculated a C_{2v} geometry with r(Br–O)=1.80902 Å and a bond angle of 115.69°. This calculation yielded a shorter bond distance but a larger bond angle than the work of [90LEV/OGD] and was stated to be due to the exclusion of electron correlation in the calculation.

Jacox [84JAC], [90JAC], [94JAC], in her reviews, recommended an a_1 symmetric stretch of 526.1 cm^{-1} (Ar) based on the studies by [78TEV/WAL, 87ALL/POL], and a ν_3 asymmetric stretch of 623.4 cm^{-1} (Ar) based on the work by [90LEV/OGD]. Jacox did not report a value for ν_2.

Lee [95LEE], using *ab initio* techniques, calculated the equilibrium structure and harmonic vibrational frequencies of Br_2O. The results suggested a C_{2v} symmetry with a bond angle of 112.9° and a bond distance of 1.865 Å.

Mueller and Cohen [95MUE/COH], from the microwave spectra of three isotopomers of BrOBr(g), determined r_0=1.8429 Å and a bond angle of 112.24°. Their study implied ν_2=180±5 cm^{-1}.

Novak [92NOV] estimated the enthalpy of formation, $\Delta_f H°(Br_2O, 0\ K)=83\pm 8$ kJ/mol from a sum of bond enthalpies that were deduced from the data of H_2O and HOBr. The enthalpy of formation corresponds to $\Delta_{at}H°(0\ K)=399.6$ kJ/mol or an average bond dissociation energy of roughly 200 kJ/mol. The author did not specify the temperature; we assume T/K=0.

Orlando and Burkholder [95ORL/BUR] recorded the UV/visible absorption spectra and observed maxima near 200 nm and 314 nm. They also determined the equilibrium constant for the reaction $Br_2O+H_2O \rightarrow 2HOBr$, K=0.02. Using auxiliary data, [95ORL/BUR] derived $\Delta_f H(Br_2O, 298\ K)$ =138 kJ/mol.

Thorn *et al.* [95THO/MON] quoted the enthalpy of formation value derived by [95ORL/BUR] to encompass the range of 113–159 kJ/mol. From a study of the photoionization efficiency spectrum of Br_2O, along with the ionization energy and the appearance energy of BrO^+, the authors derived $\Delta_f H(Br_2O, 298\ K)=107.1$ kJ/mol and $\Delta_f H(Br_2O, 0\ K)$ =124.1 kJ/mol. The uncertainty was estimated to be ±3.5 kJ/mol.

Lee [95LEE], using the CCSD(T) electron correlation method in conjunction with the basis set of triple zeta double polarized (TZ2P) quality, calculated the enthalpy of formation of Br_2O. The author reported a value of 33 kcal/mol at 0 K (138 kJ/mol).

5.7. Br_2O (BrBrO)

There are no gas phase spectroscopic studies on this molecule. All experimental work is in the condensed phase???: pure solid and isolated in an argon matrix. The reviews by Jacox [84JAC], [90JAC], [94JAC] summarized these structural and spectroscopic studies in which two of the three vibrations have been observed. The structure and vibrational frequencies of this molecule are summarized in Table 6.

There are numerous articles which provide specific spectroscopic information:

(1) Reaction complex OBrBr follows the $O+Br_2$ reaction - [73DIX/PAR], [73PAR/HER]
(2) Infrared spectra in an argon matrix [78TEV/WAL]
(3) Structure in an argon matrix [80VEL/DUR], [82FER/SMI], [87LOE/AND]
(4) Reactive scattering of oxygen atoms with chlorine molecules; observed results which are consistent with OClCl with a $^3\Pi$ symmetry when colinear and $^3A''$ symmetry when bent. Browett *et al.* [81BRO/HOB] referred to the analogous O–X–X study as described by [78TEV/WAL] and [73PAR/HER]
(5) The vibrational frequency information (ν_1, ν_3) was reviewed by Jacox [84JAC], [90JAC], [94JAC] and was based on the data reported by [78TEV/WAL]
(6) [93SCH/ABD] used Fourier transform infrared (FTIR) techniques to study BrBrO in an argon matrix; their observations supported the conclusions of Tevault *et al.* [78TEV/WAL]
(7) Burdett *et al.* [84BUR/LAW], in a review, discussed the stability and spectroscopic properties of BrBrO but referred back to the work of [78TEV/WAL] as the only source of information
(8) Lee [95LEE], using *ab initio* techniques, calculated the equilibrium structure and harmonic vibrational frequencies of BrBrO.

In examining cross beam experiments involving the collision of O atoms with bromine molecules, Parrish and coworkers [73DIX/PAR, 73PAR/HER] proposed the existence of an asymmetric OBrBr complex with the possibility of a rather substantial bond angle, 150 °C. However, neither of the two 1973 studies [73DIX/PAR, 73PAR/HER] provided definitive structural information. The kinetic studies suggested a triplet electronic ground state.

Tevault *et al.* [78TEV/WAL] studied the reaction of atomic and molecular bromine with atomic and molecular oxygen in argon matrices (photolysis of bromine and ozone containing matrices). Several bromine oxygen compounds were stated to have been formed and identified by infrared spectroscopy—BrO, OBrO, BrBrO, BrOBr, and $(BrO)_2$. The authors observed the spectra of BrBrO in a photolyzed $Ar-Br_2-O_3$ matrix. The assignments were assumed to be ν_1=804 cm^{-1} (Br–O stretch), ν_3=236 cm^{-1} (Br–Br stretch) and the ν_2 value (the bending mode) was expected to be below 200 cm^{-1}.

Veltman *et al.* [80VEL/DUR] stated that reactive scattering results were consistent with the long-lived triplet of the OBrBr configuration suggested by [78TEV/WAL].

Fernie *et al.* [82FER/SMI] proposed the existence of a short-lived OBrBr collision complex with a bent configuration and $^3A''$ symmetry with a modest well of an E_0 approximately 110 kJ/mol.

Loewenstein and Anderson [87LOE/AND] proposed the existence of a long-lived intermediate of a cyclic BrBrO structure.

Jacox [84JAC], [90JAC], [94JAC], in her reviews, recommended an a′ BrO stretch value, in argon matrix, of 804 cm^{-1} and a BrBr stretch value, in argon matrix, of 236 cm^{-1}, based on the study by [78TEV/WAL]. Lee [95LEE], using *ab initio* techniques, calculated an enthalpy of formation at 0 K of 47.4 kcal/mol (198.3 kJ/mol).

5.8. Br_2 [O_2]

This oxide has been proposed as an activated complex to aid in the description of kinetic processes. Although the majority of experimental studies which refer to Br_2O_2 were in aqueous solutions, there were some gas phase studies. In addition, there were two spectroscopic studies in which an absorption was attributed to Br_2O_2. Tevault *et al.* [78TEV/WAL] tentatively identified a molecule as $(BrO)_2$ through oxygen-18 isotopic enrichment experiments in argon matrices. They suggested that the most likely structures were an open chain such as OBr–BrO and BrOBrO. Mauldin *et al.* [93MAU/WAH], in their study of the self-reaction of the BrO radical, attributed an absorption structure to Br_2O_2, but assumed a Br–O–O–Br structure.

Epiolis *et al.* [84EPI/LAS] listed this species in tables (with many related molecules), but there were no structural data provided. The article implied that calculations could have been made on this species, but there was absolutely no mention of this species in their discussion.

The pertinent articles may be grouped as follows:

1. Proposed intermediate in aqueous solution -
   [30BRA], [34SKR], [52EDW], [58SIG], [68BUK/DAI], [68EDW/GRE], [72FIE/KOR], [73SOK/DOR], [76HER/SCH], [78ROV/ZHA], [79NOS/BOD], [86THO]
2. Proposed as intermediate in gas phase reaction systems -
   [70BRO/BUR], [70CLY/CRU], [80JAF/MAI], [81SAN/WAT], [83BUT/MOR], [86SAN], [90TUR/BIR], [93MAU/WAH]
3. Proposed structure -
   [30BRA]: BrOOBr or OBrBrO (possible)
   [52EDW]: Donor-acceptor intermediate $BrBrO_2$
   [66SPR/PIM]: Calculation, BrOOBr (staggered or trapezoidal)
   [68EDW/GRE]: $BrBrO_2$
   [70CLY/CRU]: Symmetric planar bent BrOOBr (120°)
   [73SOK/DOR]: BrOOBr
   [78TEV/WAL]: Possibly OBr-BrO or BrOBrO
   [80JAF/MAI]: Possibly staggered or trapezoidal (Br-O-O-Br)
   [81SAN/WAT]: Trapezoidal (Br-O-O-Br)
   [86THO]: BrOOBr
   [90TUR/BIR]: BrOOBr
   [93MAU/WAH]: BrOOBr
4. Spectroscopy -
   [78TEV/WAL], [93MAU/WAH]

5.9. Br_2O_3 (OBrOBrO)

The citations listed in the bibliography for Br_2O_3 can be classified as follows:

1. Dissertations (full copy not available at this time) -
   [66CAM], [78PAS], [83ALL]
2. Formation with crystal characterization -
   [74PAS/PAV], [76PAS/PAV], [77PAS/PAV], [94LEO/SEP]
3. Comment/formation without characterization -
   [87ALL/POL]
4. Patent (lubricants) -
   [84STE]

The status of the characterization of solid Br_2O_3 is best summarized by statements provided by Allen *et al.* [87ALL/POL]: "There has also been considerable work on the vibrational spectra of the solid higher oxides of bromine (Br_2O_3, Br_2O_4), but structural conclusions had to be somewhat tentative." Pascal *et al.* [74PAS/PAV] prepared Br_2O_3 by the thermal decomposition of Br_2O_4. The authors stated that the vibrational spectrum of Br_2O_3 shows the presence of a BrOBr bond, but that it was not possible to distinguish between structural possibilities: OBrOBrO and $BrOBrO_2$. Chemical analysis established the stoichiometry. Br_2O_3 was said to be a stable intermediate in the decomposition of Br_2O_4 to Br_2O. A subsequent study [76PAS/PAV], using Raman spectra, indicated that the structure was OBrOBrO. At a conference, these same authors [77PAS/PAV] summarized their work by discussing the synthesis of the two isomers of Br_2O_4, Br_2O_3, and Br_2O in a Raman tube and the spectra obtained at 93 K. The stepwise decomposition of Br_2O_4 to Br_2O was presented and vibrational frequencies assigned. In summary, analysis of the vibrational spectra of the crystalline phase by Pascal *et al.* [76PAS/PAV, 77PAS/PAV] of the various possible isomers of Br_2O_3 and Br_2O_4, suggested that Br_2O_3 has the structure (OBrOBrO) and that the two Br_2O_4 isomers have the structure (O_2BrBrO_2) and ($O_2BrOBrO$).

Leopold and Seppelt [94LEO/SEP] stated that because of the similarity of Raman spectra, the Br_2O_3 identified by [74PAS/PAV] is probably identical with the Br_2O_3 investigated by the crystal structure analysis of [93KUS/SEP] (see Sec. 5.10).

Allen *et al.* [87ALL/POL] studied the condensation of O_3/Ar and Br_2/Ar mixtures. The IR spectrum was interpreted to suggest the formation of a Br_2/O_3 complex. However, the structure could not be unambiguously determined.

5.10. $BrOBrO_2$ ($Br^+BrO_3^-$)

Kuschel and Seppelt [93KUS/SEP, 93STI] prepared Br_2O_3 by the reaction of bromine with ozone at −50 to −60 °C. The authors stated that other workers used this same reaction 35 years ago but, in contrast, characterized the product as BrO_2; the identification may have been based on impure material. Kuschel and Seppelt deduced the structure of the crystal (bond distances and bond angles) by the use of the EXAFS-method (extended x-ray absorption fine structure) and the Raman spectra.

The authors compared the structural data of their $Br^+BrO_3^-$ with that described by [92GIL/LEV] for $BrBrO_4$. The comparison suggested that these products may have been the same. Thus, there is some question raised as to the existence of $BrBrO_4$.

5.11. Br_2O_4 (O_2BrBrO_2)

There is no gas phase or thermodynamic information on this molecule, however, some crystalline data (structure and vibrational frequencies) are available. Of the eight articles, the studies can be grouped as follows:

1. Formation and characterization - [73PAS/POT], [74PAS/PAV], [76PAS/PAV], [77PAS/PAV], [87ALL/POL], [94LEO/SEP]
2. Intermediate in solution - [80FOE/LAN], [83FIE/RAG], [91SZA/WOJ].

Pascal and Potier [73PAS/POT] interpreted the Raman spectrum of the BrO_2 crystalline form (−180 °C) in terms of a dimeric structure with a Br–Br bond. They specifically ruled out a chain or ring structure with bridging oxygen atoms. Tentative assignments were made for some of the observed frequencies. In a subsequent study [74PAS/PAV] of the vibrational spectra of Br_2O_3, the authors discussed the corresponding spectra of Br_2O_4 and suggested the structure to be O_2BrBrO_2. In studying the reaction between ozone and Br_2O_3, Pascal *et al.* [76PAS/PAV, 77PAS/PAV] observed two isomers of Br_2O_4. The asymmetric isomer [$O_2BrOBrO$], was not isolated and rapidly transformed to the symmetric isomer [O_2BrBrO_2]. An analysis of the vibrational spectra of the various possible isomers of Br_2O_3 and Br_2O_4 suggested that Br_2O_3 has the structure (OBrOBrO) and that the two Br_2O_4 isomers have the structure (O_2BrBrO_2) and (O $_2$BrOBrO). Some tentative spectral assignments have been made. [94LEO/SEP] questioned the existence of this compound.

Allen *et al.* [87ALL/POL] mentioned the formation and characterization of Br_2O_4 but did not perform any additional work on this species.

The dimerization of BrO_2 to Br_2O_4 was proposed to explain aqueous reaction kinetics:

(1) The Belousov-Zhabotinsky-system-($HBrO_2$)/BrO_3^- reaction [80FOE/LAN],
(2) The pulse radiolysis of the bromine dioxide radical and hexacyanoferrate (4−), manganese (II), phenoxide ion, or phenol [83FIE/RAG], and
(3) The pulse radiolysis of the hexacyanoferrate (II)-bromate cyanide system in aqueous ethylene glycol [91SZA/WOJ].

5.12. $O_2BrOBrO$

There is no gas phase or thermodynamic information on this molecule, however, some crystalline data (structure and vibrational frequencies) are available. All three articles can be classified as formation and characterization: [74PAS/PAV], [76PAS/PAV] and [77PAS/PAV].

In attempting to study Br_2O, Pascal *et al.* have examined the decomposition of Br_2O_4 and the formation of an intermediate Br_2O_3. In the analysis of the vibrational spectra of Br_2O_3, [74PAS/PAV] discussed the corresponding spectra of Br_2O_4 and suggested the structure to be O_2BrBrO_2. Subsequent studies by Pascal *et al.* [76PAS/PAV, 77PAS/PAV] prepared two isomers of Br_2O_4. These authors observed a slow reaction between ozone and Br_2O_3. The asymmetric isomer [$O_2BrOBrO$] formed was not isolated and rapidly transformed to the symmetric isomer [O_2BrBrO_2]. An analysis of the vibrational spectra of the various possible isomers of Br_2O_3 and Br_2O_4 suggested that Br_2O_3 has the structure (OBrOBrO) and that the two Br_2O_4 isomers have the structure (O_2BrBrO_2) and ($O_2BrOBrO$). Some tentative spectral assignments have been made. [94LEO/SEP] questioned the existence of this compound.

5.13. $BrBrO_4$

Gilson *et al.* [92GIL/LEV] discussed the formation of $BrBrO_4$ by passing a mixture of bromine and oxygen through a discharge tube. The authors were surprised that with the hydrolysis of the yellow solid, BrO_4^- was identified in the solution. Bromine K-edge EXFAS data on this solid detected vibrations which were assignable to a Br–O–Br bridge. This is in contrast to the results of [73PAS/POT]. Three distinct shells were observed corresponding to terminal Br-O, bridging Br–O, and nonbonded Br–Br distances at 1.61(2), 1.86(2), and 3.05(3) Å respectively, concomitant with the proposed structure. A Br–O–Br bridging angle of 110±3° was calculated by triangulation. [94LEO/SEP] supported the existence of this isomer.

5.14. Br_2O_5

Of the 13 articles, the studies can be classified as follows:

1. Patent (cellulose esterification) - [47PRA]
2. Preparation - [39SCH/WIE], [58ARV/AYM], [59ARV/AYM], [59PFL], [59SCH]
3. Review - [63SCH/BRA]
4. Formation with characterization - [76PAS/PAV2], [77PAS/PAV], [94LEO/SEP]
5. Misclassified (really deal with BrO) - [88BAR/BOT] and [88COS/TEN], and
6. Archeology/vitrified slag (uncharacterized) - [88FLE/SWA] and [90HAR/WHI].

Arvia *et al.* [58ARV/AYM, 59ARV/AYM] studied the thermal reaction between bromine and ozone. Under different conditions, they observed Br_2O_5 and Br_3O_8. The authors specifically stated that BrO_3 or Br_2O_6 was not observed, contrary to the result of Pflugmacher. Pflugmacher [59PFL] and Schumacher [59SCH] responded to this article and further discussed possible interpretations of the results. These studies do not conclusively suggest the existence of Br_2O_5.

Pascal *et al.* [76PAS/PAV2] recorded the Raman spectra of the white solid Br_2O_5. The authors deduced that the structure ($O_2BrOBrO_2$) was a symmetric, polymeric structure similar to I_2O_5. Comparison of the observed Raman spectra with that known for the ions bromite, bromate and perbromate resulted in the identification of vibrations which were attributed to a bromine-terminal oxygen and a -bridging oxygen. Additional assignments were presented by the authors to justify their selection of the structure. In a later study, [77PAS/PAV] suggested that in the reaction of ozone with bromine, whenever Br_2O_5 was formed, it was always mixed with Br_2O_3 or Br_2O_4. The authors continued to propose a polymeric structure (for Br_2O_5) analogous to that of I_2O_5.

Leopold and Seppelt [94LEO/SEP] presented a crystal structure analysis which characterized Br_2O_5 which crystallized with three molecule propionitrile. The structure was depicted as $O_2BrOBrO_2$. The Raman spectra of solvate-free Br_2O_5 was in agreement with this structure. The Raman spectra determined by [94LEO/SEP] differs from that by [76PAS/PAV2].

5.15. Br_2O_6

The available information does not conclusively confirm the existence of Br_2O_6. The nine articles listed in the bibliography refer to the preparation of the condensed phase oxide Br_2O_6 (or BrO_3). All articles involved the reaction of ozone with bromine, except Mungen and Spinks [40MUN/SPI] who were actually investigating the decomposition of ozone. No property data have been reported. There is no gas phase information.

Schwarz and Wiele [38SCH/WIE] studied the thermal decomposition of BrO_2. In addition to the formation of the elements, the authors also detected a white oxide which they presumed was Br_2O_7 or Br_2O_6 and a dark-brown oxide, Br_2O. Schwarz and Wiele [39SCH/WIE] continued their study of the thermal decomposition of BrO_2. Their study showed that BrO_2 is completely stable at −40 °C, but that decomposition can be detected manometrically. BrO_2 sublimes with extensive decomposition, melting in dry air at approximately −17.5 °C. Br_2O is stable at −40 °C. Again Br_2O_7 was suggested as one of the decomposition products of BrO_2.

Pflugmacher *et al.* [55PFL, 55PFL/RAB], in studying the reaction of Br_2 and O_2 in a glow discharge, stated that the product was BrO_3 (or Br_2O_6) but did not isolate the compound.

Arvia *et al.* [59ARV/AYM, 59ARV/AYM] studied the thermal reaction between bromine and ozone. Under different conditions, they observed Br_2O_5 and Br_3O_8. The authors specifically stated that BrO_3 or Br_2O_6 was not observed, contrary to the result of Pflugmacher. Pflugmacher [59PFL] and Schumacher [59SCH] responded to this article and further discussed possible interpretations of the results. Refer to Sec. 5.4 on BrO_3 for additional information.

5.16. Br_2O_7

Although two articles allude to the formation of the heptoxide [38SCH/WIE, 39SCH/WIE], no definitive information is available to confirm its existence. At this time, we assume that such an oxide does not exist, as suggested by [55PFL, 55PFL/RAB].

Schwarz and Wiele [38SCH/WIE] studied the thermal decomposition of BrO_2. In addition to the formation of the elements, the authors also detected a white oxide which they presumed was Br_2O_7 or Br_2O_6 and a dark-brown oxide, Br_2O. Schwarz and Wiele [39SCH/WIE] continued their study of the thermal decomposition of BrO_2. Their study showed that BrO_2 is completely stable at −40 °C, but that decomposition can be detected manometrically. BrO_2 sublimes with extensive decomposition (to Br_2), melting in dry air at approximately −17.5 °C. Br_2O is stable at −40 °C. Again Br_2O_7 was suggested as one of the intermediate decomposition products of BrO_2. According to Pflugmacher [55 PFL, 55PFL/RAB], Br_2O_7 probably did not exist.

5.17. Br_3O_8

There are numerous pre-1960 studies which mention the preparation of a presumed condensed phase oxide with the composition Br_3O_8. Although 28LEW/SCH, 29LEW/SCH, 29LEW/SCH2, and 30LEW/SCH discussed the preparation of this oxide, 55PFL, 55PFL/RAB, 58ARV/AYM, and 59ARV/AYM repeated the procedure and determined that the product was BrO_3 (or Br_2O_6) not Br_3O_8. No property information is available. Based on existing information, there is no conclusive evidence that this compound exists.

Of the articles published since 1975 and indexed (by CAS) to this oxide, only three (of which two are both patents) may deal with Br_3O_8. The other four, in fact, deal with BrO in the stratosphere and troposphere, and are misclassified.

All citations can be grouped into five categories.

1. Patent -
   [90JOO] and [91BEN/GER]
2. Misclassified as Br_3O_8 (really BrO) -
   [89BRU/AND], [89CAR/SAN], [90BOT/BAR], and [91MOU/JAK]
3. Review -
   [34BRA], [60GEO], [63SCH/BRA]
4. Formation/preparation/decomposition -
   [28LEW/SCH], [29LEW/SCH],[29LEW/SCH2], [30LEW/SCH], [55PFL], [55PFL/RAB], [58ARV/AYM], [59ARV/AYM], [59PFL], [59SCH], [74SOL/KEI]
5. Sensitized decomposition of ozone -
   [31LEW/FEI], [31SPI], [40MUN/SPI].
6. Reaction -
   [90BIG/BRO]

When Lewis and Schumacher [28LEW/SCH] allowed bromine and ozone to mix in a flask (no temperature was specified), a white deposit appeared on the walls on the flask. This solid was thought to be an oxide of bromine, later described as Br_3O_8. Shortly after the formation of the solid, an explosion destroyed the apparatus. In subsequent work by Lewis and Schumacher [29LEW/SCH] at low temperatures, −5 to 10 °C, an oxide of bromine was formed which had the composition Br_3O_8 and existed in two crystalline modifications. Two subsequent studies by the same authors [29LEW/SCH, 29LEW/SCH2] examined the thermal reaction in more detail to observe the formation and the rate of decomposition. The transition temperature between the two presumed crystalline forms was determined to be -35 ± 3 °C. The thermal reaction between bromine and ozone was studied again in 1930 [30LEW/SCH] to determine the kinetics of decomposition.

In a review article, Brady [34BRA] mentioned that the method used by Lewis and Schumacher [29LEW/SCH] to obtain Br_3O_8, was used by Zintl and Rienacker [30ZIN/RIE] for the preparation of Br_2O [refer to the Br_2O discussion for these references]. The implication is that Br_3O_8 is not a pure, single compound.

Arvia *et al.* [58ARV/AYM, 59ARV/AYM] studied the thermal reaction between bromine and ozone. Under different conditions, they observed Br_2O_5 and Br_3O_8. The authors specifically stated that BrO_3 or Br_2O_6 was not observed, contrary to the result of Pflugmacher. Pflugmacher [59PFL] Schumacher [59SCH] responded to this article and further discussed possible interpretations of the results.

In the 1960 review by George [60GEO], the author stated that the proposal of a BrO_3 oxide raises doubt about the authenticity of Br_3O_8.

The 1963 review by Schmeisser and Brandle [63SCH/BRA] discussed the numerous experimental studies which led to the presumed formation of Br_3O_8. The authors also referred to other related studies which stated the product really was Br_2O_5. It appears that the reaction of bromine with ozone can lead to a mixture of different bromine oxides. In addition, part of the problem may lie in the precise characterization of the products.

6. NIST JANAF Thermochemical Tables

NIST-JANAF Thermochemical Tables for BrO(g) (Sec. 6.1), OBrO(g) (Sec. 6.2), BrOO(g) (Sec. 6.3), BrO_3(g) (Sec. 6.4), BrOBr(g) (Sec. 6.5), and BrBrO(g) (Sec. 6.6) are presented on the following pages.

$D_0^\circ = 19332 \pm 200\ cm^{-1}$
$S^\circ(298.15\ K) = 232.97 \pm 0.1\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H^\circ(0\ K) = 133.3 \pm 2.4\ kJ \cdot mol^{-1}$
$\Delta_f H^\circ(298.15\ K) = 125.8 \pm 2.4\ kJ \cdot mol^{-1}$

Electronic Levels and Molecular Constants ($^{79}Br^{16}O$), cm^{-1}

State	T_e	g_i	ω_e	$\omega_e x_e$	$\omega_e y_e$	B_e	α_e	$D_e \cdot 10^6$	r_e/Å
$X^2\Pi_{3/2}$	0	2	727.05	4.932	–	0.4299	0.003639	0.594	1.717
$X^2\Pi_{1/2}$	968	2	727.05	4.932	–	0.4299	0.003639	0.594	1.717
$A^2\Pi_{3/2}$	27871	2	511.3	4.83	−0.074	0.314	0.0034	0.474	1.95
$A^2\Pi_{1/2}$	[29321]	2	511.3	4.8	−0.074	0.314	0.0034	0.474	1.95

Point Group: $C_{\infty v}$ $\sigma = 1$

Enthalpy of Formation

The two existing spectroscopic studies by Coleman and Gaydon[1] and Durie and Ramsay[2] yield dissociation energy values for BrO(g). One should note, with respect to those studies, that the first bound excited state $A^2\Pi$ of BrO(g) dissociates to $Br(^2P_{3/2}) + O(^1D_2)$. A linear Birge–Sponer extrapolation of the Coleman and Gaydon[1] data gave 17800 cm^{-1} or 213.2 $kJ \cdot mol^{-1}$ for the ground state dissociation energy. Assuming the extrapolation was high by up to 20%, they recommended 1.75 ± 0.3 eV or $170 \pm 29\ kJ \cdot mol^{-1}$. Durie and Ramsay,[2] from a graphical Birge–Sponer extrapolation, calculated a dissociation energy of $D_0^\circ = 19332 \pm 200\ cm^{-1}$ or $231.6 \pm 2.4\ kJ \cdot mol^{-1}$. The latter value leads to the present adopted value for $\Delta_f H^\circ(298.15\ K)$ for BrO(g) of $125.8 \pm 2.4\ kJ \cdot mol^{-1}$. Additional data needed for the calculations presented here, e.g. thermal functions for the Br(g), and Br_2(ref), O(g), and O_2(ref), are taken from the JANAF Thermochemical Tables.[3]

Heat Capacity and Entropy

The spectroscopic results tabulated above are for the $^{79}Br^{16}O$ isotopomer. Isotopic relationships[4] are used to convert the above constants to those for the normally occurring, i.e. natural abundance, species. The latter values are then used in the calculation of the thermal functions. Only the X and A states are included in the calculation of the thermal functions; a sum-over-states technique is used.

Values of ω_e and $\omega_e x_e$ given in the table above for the ground state are from Butler *et al.*,[5] while those for the first excited state are from Barnett *et al.*[6] These values in fact described an average $^2\Pi$ state; there are differences in the vibrational constants for the $X^2\Pi_{3/2}$ and $X^2\Pi_{1/2}$ states but they are not considered in this calculation. The B_e value for the ground state is from Amano *et al.*[7] The internuclear distance and value for B_e for the A state are from Barnett *et al.*[6] The value of D_e for the excited state was estimated.[4] Barnett *et al.*[6] gave a dissociation energy of 8960 cm^{-1} for the A state which is used in conjunction with T_e to provide an energy cutoff from the sum-over-states calculation on the excited state.

Previously, the value of the spin orbit constant, A_o, for the inverted doublet $X^2\Pi$ ground state adopted by Huber and Herzberg[8] was an average based on two values derived from the EPR spectra studies: $A_o = -815\ cm^{-1}$ of Carrington *et al.*[9] and $A_o = -980\ cm^{-1}$ of Brown *et al.*[10] The recent measured value of McKellar,[11] $A_o = -968\ cm^{-1}$, for the spin–orbit splitting of the ground state is adopted here. For ClO the spin–orbit splitting of the A state is approximately 1.5 times the value found for the ground state.[12] Using the same factor of 1.5, the spin–orbit splitting for the A state in BrO is estimated to be 1450 cm^{-1}.

Numerous excited states have been estimated by Monks *et al.*[13] and observed by Duignan and Hudgens.[14] These states are not fully characterized in terms of vibrational and rotational constants and do not contribute significantly to the thermal functions below 6000 K.

References

[1] E. H. Coleman and A. G. Gaydon, Discussions Faraday Soc. (2), 166 (1947).
[2] R. A. Durie and D. A. Ramsay, Can. J. Phys. **36**, 35 (1958).
[3] JANAF Thermochemical Tables: Br(g), June 1982; Br_2(ref), June 1982; O(g), Sept. 1982; O_2(ref), Sept. 1982.
[4] G. Herzberg, Spectra of Diatomic Molecules, D. Van Nostrand Co., New York, p. 107 (1950).
[5] J. E. Butler, K. Kawaguchi and E. Hirota, J. Mol. Spectrosc. **104**(2), 372–9 (1984).
[6] M. Barnett, E. A. Cohen and D. A. Ramsay, Can. J. Phys. **59**(12), 1908–16 (1981).
[7] T. Amano, A. Yoshinaga and E. Hirota, J. Mol. Spectrosc. **44**(33), 594–8 (1972).
[8] K. P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules.
[9] A. Carrington, P. N. Dyer and D. H. Levy, J. Chem. Phys. **52**(1), 309–14 (1970).
[10] J. M. Brown, C. R. Byfleet, B. J. Howard, and D. K. Russell, Mol. Phys. **23**(3), 457–68 (1972).
[11] A. R. W. McKellar, J. Mol. Spectrosc. **86**(1) 43–54 (1981).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

T/K	C_p° (J·K⁻¹mol⁻¹)	S° (J·K⁻¹mol⁻¹)	$-[G^\circ - H^\circ(T_r)]/T$ (J·K⁻¹mol⁻¹)	$H^\circ - H^\circ(T_r)$ (kJ·mol⁻¹)	$\Delta_f H^\circ$ (kJ·mol⁻¹)	$\Delta_f G^\circ$ (kJ·mol⁻¹)	log K_f
0	0.0	0.0	INFINITE	−9.061	133.305	133.305	INFINITE
50	29.103	179.334	331.631	−7.615	133.611	129.149	−134.918
100	29.139	199.511	261.104	−6.159	133.358	124.765	−65.169
150	29.592	211.388	242.681	−4.694	132.932	120.555	−41.980
200	30.805	220.050	235.985	−3.187	132.424	116.505	−30.427
250	32.493	227.101	233.523	−1.606	131.869	112.588	−23.523
298.15	34.182	232.970	232.970	0.000	125.770	109.582	−19.198
300	34.244	233.182	232.971	0.063	125.736	109.482	−19.062
400	37.062	243.447	234.351	3.638	110.586	107.200	−13.999
500	38.719	251.915	237.042	7.436	111.008	106.307	−11.105
600	39.525	259.055	240.132	11.354	111.486	105.321	−9.169
700	39.839	265.176	243.283	15.325	111.960	104.256	−7.780
800	39.901	270.502	246.360	19.313	112.405	103.125	−6.733
900	39.846	275.199	249.308	23.301	112.808	101.940	−5.916
1000	39.746	279.392	252.111	27.281	113.170	100.713	−5.261
1100	39.634	283.175	254.766	31.250	113.493	99.451	−4.722
1200	39.528	286.619	257.279	35.208	113.780	98.162	−4.273
1300	39.437	289.779	259.659	39.156	114.036	96.850	−3.891
1400	39.361	292.699	261.916	43.096	114.265	95.519	−3.564
1500	39.301	295.412	264.060	47.029	114.467	94.173	−3.279
1600	39.256	297.947	266.099	50.957	114.647	92.814	−3.030
1700	39.225	300.326	268.043	54.881	114.805	91.445	−2.810
1800	39.205	302.568	269.900	58.802	114.942	90.066	−2.614
1900	39.194	304.687	271.675	62.722	115.057	88.681	−2.438
2000	39.189	306.697	273.377	66.641	115.153	87.291	−2.280
2100	39.189	308.609	275.009	70.560	115.226	85.895	−2.136
2200	39.189	310.432	276.578	74.479	115.279	84.497	−2.006
2300	39.188	312.174	278.088	78.398	115.310	83.098	−1.887
2400	39.182	313.842	279.544	82.316	115.318	81.697	−1.778
2500	39.168	315.441	280.948	86.234	115.303	80.296	−1.678
2600	39.145	316.977	282.304	90.150	115.264	78.897	−1.585
2700	39.110	318.454	283.616	94.062	115.201	77.498	−1.499
2800	39.061	319.875	284.886	97.971	115.112	76.103	−1.420
2900	38.996	321.245	286.116	101.874	114.998	74.711	−1.346
3000	38.915	322.566	287.309	105.770	114.858	73.325	−1.277
3100	38.817	323.840	288.467	109.656	114.690	71.945	−1.212
3200	38.701	325.071	289.592	113.532	114.496	70.568	−1.152
3300	38.568	326.260	290.685	117.396	114.276	69.198	−1.095
3400	38.418	327.409	291.748	121.245	114.028	67.836	−1.042
3500	38.251	328.520	292.783	125.079	113.755	66.483	−0.992
3600	38.068	329.595	293.791	128.895	113.453	65.136	−0.945
3700	37.871	330.635	294.773	132.692	113.124	63.796	−0.901
3800	37.661	331.643	295.730	136.469	112.769	62.471	−0.859
3900	37.439	332.618	296.663	140.224	112.389	61.150	−0.819
4000	37.205	333.563	297.574	143.956	111.980	59.840	−0.781
4100	36.963	334.479	298.463	147.665	111.547	58.545	−0.746
4200	36.712	335.366	299.331	151.349	111.088	57.255	−0.712
4300	36.454	336.227	300.179	155.007	110.603	55.980	−0.680
4400	36.191	337.062	301.008	158.639	110.093	54.717	−0.650
4500	35.924	337.873	301.818	162.245	109.559	53.463	−0.621
4600	35.654	338.659	302.611	165.824	108.999	52.222	−0.593
4700	35.382	339.423	303.386	169.376	108.416	50.994	−0.567
4800	35.108	340.165	304.144	172.900	107.809	49.780	−0.542
4900	34.835	340.886	304.887	176.397	107.177	48.579	−0.518
5000	34.562	341.587	305.614	179.867	106.523	47.388	−0.495
5100	34.291	342.269	306.326	183.310	105.844	46.213	−0.473
5200	34.021	342.932	307.024	186.725	105.143	45.048	−0.452
5300	33.755	343.578	307.707	190.114	104.418	43.900	−0.433
5400	33.491	344.206	308.377	193.476	103.669	42.765	−0.414
5500	33.232	344.818	309.034	196.813	102.898	41.646	−0.396
5600	32.976	345.415	309.679	200.123	102.103	40.537	−0.378
5700	32.724	345.996	310.311	203.408	101.285	39.445	−0.361
5800	32.477	346.563	310.931	206.668	100.444	38.367	−0.346
5900	32.235	347.116	311.540	209.903	99.579	37.305	−0.330
6000	31.998	347.656	312.137	213.115	98.690	36.256	−0.316

PREVIOUS CURRENT: March 1996 (1 bar)

Bromine Oxide (OBrO) | Ideal Gas | M_r = 111.9028

$\Delta_a H°(0\ K) = [450 \pm 25]\ kJ \cdot mol^{-1}$
$S°(298.15\ K) = [271.1 \pm 2]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [161.5 \pm 25]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [152.0 \pm 25]\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight

State	ϵ_i, cm^{-1}	g_i
X^2B_1	0.0	2

Vibrational Frequencies and Degeneracies

ν, cm^{-1}
800 (1)
300 (1)
852 (1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: Br–O = 1.649 Å
Bond Angle: O–Br–O = 114.4°
Product of the Moments of Inertia: $I_A I_B I_C = 409.0844 \times 10^{-117}\ g^3 cm^6$

Enthalpy of Formation

For the series OXO(g) [where X = F, Cl, Br, I], there is only reliable experimental data for OClO(g). Assuming that the values $\Delta_a H°$(OClO,g) and $D_0°$(ClO) are reasonable, we adopt the ratio of the numbers (~1.94) to apply for a similar relationship between BrO(g) and OBrO(g). Thus we calculate $\Delta_a H°$(OBrO, g, 0 K) = 1.94×$D_0°$ (BrO) = 450 ± 25 kJ·mol^{-1}.

Cottrell[1] reported D(O–BrO) ≥ 70 ± 10 kcal·mol^{-1}. This converts to $\Delta_f H°$(0 K) = 87 kJ·mol^{-1}. This value was based on the enthalpy of formation of BrO_2(cr) reported by Pflugmacher *et al.*[2] and a $D_0°$(BrO) = 2.25 eV or 52 kcal·mol^{-1}. Cottrell expressed doubt as to the validity of this value based on comparison with ClO_2. The enthalpy of dissociation reported by Vedeneyev *et al.*[3] was ΔH(298 K) ≥ 70 kcal·mol^{-1} for the reaction $BrO_2 \rightarrow BrO + O$. This is an estimated value based on the work by Cottrell (1954) although a different temperature was given.

In contrast, Huie and Laszlo[4] have estimated the enthalpy of formation of OBrO(g) in the following manner. According to Stanbury,[5] the enthalpy of formation of OBrO in the gas phase can be estimated by assuming that the difference in the $\Delta_f G$ for Cl_2(g) and ClO_2(aq) also applies for the bromine species. Using a value of 2.9 kJ·mol^{-1} recommended by Wagman *et al.*[6] as this difference and $\Delta G(BrO_2, aq)$ = 144.0 kJ·mol^{-1}, we obtain $\Delta G°$ = 146.9 kJ·mol^{-1} for OBrO(g) and $\Delta_f H°$ = 122.5 kJ·mol^{-1}. In comparison $D_0°$(BrO) = 231.6 kJ·mol^{-1}.

Heat Capacity and Entropy

Mueller *et al.*[7] have measured the microwave spectra of OBrO(g). Preliminary analysis of the data suggested a bent structure (r_0 = 1.649 Å and <(OBrO) = 114.4°). This structure is adopted and is consistent with the expected trends in the corresponding chlorine and iodine oxide molecules. The principal moments of inertia (in g cm^2) are: $I_A = 3.0275 \times 10^{-39}$, $I_B = 10.2087 \times 10^{-39}$, and $I_C = 13.2361 \times 10^{-39}$.

In support of this study, Byberg and Spanget-Larsen[8] used modified extended Huckel theory to calculate nuclear quadrupole coupling constants for a series of oxygen halogen compounds. The comparison of calculated values with observed values helped confirm the geometry of BrO_2: C_{2v} symmetry with a bond length of 1.625 Å and a bond angle of 117.6°. This geometry was assumed to be similar to that of ClO_2, using a 0.15 Å difference between the covalent radii of the chlorine and bromine atoms.

Tevault *et al.*[9] observed the infrared spectra of BrO_2 in a solid argon matrix. Assuming the proper identification of the antisymmetric stretching ν_3 to be 852 cm^{-1}, the apex angle was calculated to be 110 ± 2°. This was close to the value observed for the analogous matrix isolated ClO_2.

The recommended vibrational frequency (ν_3) is that suggested by Jacox.[10] This data is based on the infrared spectra of the argon matrix isolated radical as studied by Tevault *et al.*[9] Preliminary microwave studies by Mueller *et al.*[7] suggested an approximate value for ν_2 (300 cm^{-1}). The unobserved vibrational frequency (ν_1) is estimated from those which describe the other halogen oxide molecules.[11] Maier and Bothur,[12] using flash photolysis, trapped OBrO in a matrix and measured ν_1 and ν_3 for two isotopes. Their values for ν_3 are within a few wave numbers of the values derived by Tevault *et al.*[9] ν_1 values are of the order of 791–799 cm^{-1}, depending on the concentration of the pyrolized mixture ($Br_2/O_2/Ar$).

References

[1] T. L. Cottrell, The Strengths of Chemical Bonds, Butterworths, London, 221–81 (1954).
[2] A. Pflugmacher, R. Schwarz and H. J. Rabbin, Z. anorg. u. allgem. Chem. **264**, 204–8 (1951).
[3] V. I. Vedeneyev, L. V. Gurvich, V. N. Koncrat'yev, V. A. Medvedev and Ye. L. Frankevich, Bond Energies, Ionization potentials and Electron Affinities, Arnold, London, 78–130 (1966).
[4] R. Huie and B. Laszlo, Adv. Chem. Series, in press (1995).
[5] D. M. Stanburry, Adv. Inorg. Chem. **33**, 69–138 (1989).
[6] D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, and S. M. Bailey, NBS-TN-270-3, 31 (1968).
[7] H. S. P. Mueller, C. Miller and E. A. Cohen, submitted for publication in Angew. Chem.
[8] J. R. Byberg and J. Spanget-Larsen, Chem. Phys. Lett. **23**(2), 247 (1973).
[9] D. E. Tevault, N. Walker, R. R. Smardzewski, and W. B. Fox, J. Phys. Chem. **82**, 2733 (1978).
[10] M. E. Jacox, J. Phys. Chem. Ref. Data, Monograph No. 3, 461 pp. (1994).
[11] JANAF Thermochemical Tables: OClO(g): Sept. 1995; OIO: Sept. 1995.
[12] G. Maier and A. Bothur, Z. anorg. allg. Chem. **621**, 743–46 (1995).

Bromine oxide (OBrO) Br_1O_2(g)

Enthalpy Reference Temperature = T_r = 298.15 K; Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−11.395	161.500	161.500	INFINITE
50	33.368	204.239	398.861	−9.731	161.299	159.420	−166.544
100	35.399	227.876	308.078	−8.020	160.573	157.809	−82.431
150	37.993	242.726	283.956	−6.185	159.790	156.596	−54.531
200	40.539	254.003	275.111	−4.222	159.010	155.649	−40.651
250	43.088	263.324	271.846	−2.131	158.236	154.898	−32.364
298.15	45.364	271.112	271.112	.000	151.957	154.979	−27.152
300	45.446	271.393	271.113	.084	151.916	154.998	−26.988
400	49.171	285.010	272.944	4.826	136.447	159.211	−20.791
500	51.674	296.270	276.516	9.877	136.594	164.888	−17.226
600	53.335	305.848	280.626	15.133	136.830	170.525	−14.846
700	54.463	314.160	284.836	20.526	137.100	176.120	−13.142
800	55.253	321.487	288.969	26.015	137.375	181.675	−11.862
900	55.823	328.030	292.952	31.570	137.643	187.196	−10.865
1000	56.246	333.934	296.760	37.174	137.898	192.688	−10.065
1100	56.567	339.311	300.387	42.816	138.139	198.156	−9.410
1200	56.817	344.244	303.839	48.485	138.364	203.602	−8.863
1300	57.013	348.800	307.125	54.177	138.572	209.030	−8.399
1400	57.172	353.031	310.254	59.887	138.764	214.442	−8.001
1500	57.301	356.980	313.239	65.611	138.937	219.842	−7.656
1600	57.407	360.681	316.090	71.346	139.090	225.230	−7.353
1700	57.495	364.164	318.816	77.091	139.223	230.610	−7.086
1800	57.570	367.453	321.428	82.845	139.334	235.982	−6.848
1900	57.634	370.567	323.933	88.605	139.420	241.349	−6.635
2000	57.688	373.525	326.339	94.371	139.481	246.712	−6.443
2100	57.735	376.341	328.654	100.142	139.515	252.073	−6.270
2200	57.776	379.028	330.883	105.918	139.520	257.433	−6.112
2300	57.812	381.597	333.032	111.698	139.497	262.792	−5.968
2400	57.843	384.058	335.108	117.480	139.443	268.154	−5.836
2500	57.871	386.420	337.113	123.266	139.358	273.519	−5.715
2600	57.896	388.690	339.053	129.054	139.244	278.887	−5.603
2700	57.918	390.875	340.933	134.845	139.100	284.261	−5.499
2800	57.937	392.982	342.754	140.638	138.926	289.640	−5.403
2900	57.955	395.015	344.521	146.433	138.725	295.026	−5.314
3000	57.971	396.980	346.237	152.229	138.496	300.420	−5.231
3100	57.986	398.881	347.905	158.027	138.243	305.822	−5.153
3200	57.999	400.723	349.527	163.826	137.965	311.231	−5.080
3300	58.011	402.508	351.106	169.626	137.666	316.650	−5.012
3400	58.022	404.240	352.643	175.428	137.347	322.079	−4.948
3500	58.032	405.922	354.141	181.231	137.010	327.517	−4.888
3600	58.041	407.557	355.602	187.035	136.657	332.965	−4.831
3700	58.050	409.147	357.028	192.839	136.289	338.423	−4.778
3800	58.058	410.695	358.420	198.644	135.908	343.892	−4.727
3900	58.065	412.203	359.780	204.451	135.517	349.370	−4.679
4000	58.072	413.673	361.109	210.257	135.116	354.858	−4.634
4100	58.078	415.107	362.409	216.065	134.707	360.357	−4.591
4200	58.084	416.507	363.680	221.873	134.291	365.866	−4.550
4300	58.089	417.874	364.925	227.682	133.870	371.385	−4.511
4400	58.094	419.209	366.143	233.491	133.444	376.913	−4.475
4500	58.099	420.515	367.337	239.300	133.014	382.451	−4.439
4600	58.103	421.792	368.507	245.111	132.581	387.998	−4.406
4700	58.107	423.042	369.654	250.921	132.145	393.556	−4.374
4800	58.111	424.265	370.779	256.732	131.707	399.122	−4.343
4900	58.115	425.463	371.883	262.543	131.266	404.698	−4.314
5000	58.118	426.637	372.966	268.355	130.823	410.283	−4.286
5100	58.121	427.788	374.030	274.167	130.377	415.877	−4.259
5200	58.125	428.917	375.075	279.979	129.928	421.479	−4.234
5300	58.127	430.024	376.101	285.792	129.475	427.091	−4.209
5400	58.130	431.111	377.110	291.605	129.018	432.710	−4.186
5500	58.133	432.177	378.101	297.418	128.557	438.338	−4.163
5600	58.135	433.225	379.076	303.231	128.089	443.975	−4.141
5700	58.137	434.254	380.035	309.045	127.615	449.620	−4.120
5800	58.140	435.265	380.979	314.859	127.134	455.273	−4.100
5900	58.142	436.259	381.907	320.673	126.644	460.934	−4.081
6000	58.144	437.236	382.821	326.487	126.143	466.605	−4.062

PREVIOUS: CURRENT: March 1996 (1 bar)

Bromine oxide (OBrO) Br_1O_2(g)

$S°(298.15\ K) = [288.8 \pm 3]\ J\ K^{-1}\ mol^{-1}$

$\Delta_f H°(0\ K) = [116.1 \pm 40]\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [108.0 \pm 40]\ kJ\cdot mol^{-1}$

Electronic Level and Quantum Weight state	ϵ_i, cm^{-1}	g_i
$X[^2A'']$	0.0	[2]

Vibrational Frequencies and Degeneracies ν, cm^{-1}
1487 (1)
[250] (1)
[160] (1)

Point Group: C_s $\sigma = 1$
Bond Distances: Br–O = [2.0] Å; O–O = [1.25] Å
Bond Angle: Br–O–O = [115]°
Product of the Moments of Inertia: $I_A I_B I_C = [588.4497 \times 10^{-117}]\ g^3cm^6$

Enthalpy of Formation

Ip and Burns[1] determined the recombination rate constants of bromine atoms in the presence of six different third bodies (helium, neon, argon, krypton, oxygen and nitrogen) over the temperature range of 300 and 1273° K. The authors refer to two earlier studies: Rabinowitch and Wood[2] and Strong *et al.*[3] Based on these data, Blake *et al.*[4] calculated interaction potentials between atomic bromine, oxygen and an inert third body (such as a rare gas). A value is given for Br–O_2. BrOO was thought to be unstable with a bond energy (Br–OO) of approximately 1 kcal·mol^{-1} (at 298.15 K) which translated to an enthalpy of formation of 108.0 kJ mol^{-1}.

Heat Capacity and Entropy

Butkovskaya *et al.*[5] estimated the structure of this molecule to be bent with a Br–O–O angle of [115]° and bond lengths, r(Br–O) = [2.0] Å and r(O–O) = [1.25] Å. Butkovskaya *et al.* assumed this structure in an attempt to explain the formation of BrO_2 from the reaction of O + Br_2 in a flow discharge system. Under the experimental conditions studied, OBrO was actually formed. The principal moments of inertia (in g cm^2) are: $I_A = [1.2011 \times 10^{-39}]$, $I_B = [21.5417 \times 10^{-39}]$, and $I_C = [22.7428 \times 10^{-39}]$.

The recommended vibrational frequency for ν_1 is that suggested by Jacox.[6] In addition, we adopt ν_2=[250] and ν_3=[150] cm^{-1} based on an assumed trend of the FOO(g) and ClOO(g) vibrational frequencies.[7] ν_1 is based on the infrared spectra of the argon matrix isolated radical as studied by Tevault and Smardzewski.[8] Michael and Payne[9] calculated (BEBO method) a stretching frequency of 872 cm^{-1} for ν_1 which is in conflict with the observed frequency by Tevault and Smardzewski[8] and the corresponding value for ClOO. FOO(g) and ClOO(g) have ν_1(O–O stretch) values of 1487 and 1443 cm^{-1}, respectively.[7] Thus, ν_1=1487 cm^{-1} for BrOO appears reasonable. The authors suggested that the bending frequency of 100 cm^{-1} was consistent with their kinetic data. The recent study by Maier and Bothur[10] suggested a ν_1 value in agreement with the adopted value.

References

[1]J. K. K. Ip and G. Burns, J. Chem. Phys. **51**, 3414 (1969).
[2]E. Rabinowitch and W. C. Wood, Trans. Faraday Soc. **32**, 907 (1936).
[3]R. L. Strong, J. W. Chien, P. E. Graf, and J. E. Willard, J. Chem. Phys. **26**, 1287 (1957).
[4]D. A. Blake, R. L. Browne, and G. Burns, J. Chem. Phys. **53**, 3320 (1970).
[5]N. I. Butkovskaya, I. I. Morozov, V. L. Tal'rose, and E. S. Vasiliev, Chem. Phys. **79**, 21 (1983).
[6]M. E. Jacox, J. Phys. Chem. Ref. Data, Monograph No. 3, 461 pp. (1994).
[7]JANAF Thermochemical Tables: FOO(g), Sept. 1995; ClOO(g), Sept. 1995.
[8]D. E. Tevault and R. R. Smardzewski, J. Am. Chem. Soc. **100**, 3955 (1978).
[9]J. V. Michael and W. A. Payne, Int. J. Chem. Kinet. **11**, 799 (1979).

Enthalpy Reference Temperature = T_r = 298.15 K; Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	.000	.000	INFINITE	−12.851	116.087	116.087	INFINITE
50	35.382	212.021	435.344	−11.166	115.907	113.639	−118.718
100	41.818	238.630	330.908	−9.228	115.409	111.569	−58.278
150	45.376	256.347	303.261	−7.037	114.981	109.743	−38.216
200	47.128	269.668	293.267	−4.720	114.555	108.061	−28.223
250	48.143	280.301	289.646	−2.336	114.073	106.491	−22.250
298.15	48.875	288.845	288.845	.000	108.000	105.736	−18.524
300	48.901	289.148	288.846	.090	107.966	105.722	−18.408
400	50.265	303.404	290.781	5.049	92.714	108.119	−14.119
500	51.562	314.761	294.479	10.141	92.901	111.949	−11.695
600	52.707	324.266	298.672	15.356	93.097	115.741	−10.076
700	53.657	332.465	302.928	20.676	93.293	119.499	−8.917
800	54.421	339.682	307.080	26.082	93.485	123.230	−8.046
900	55.031	346.128	311.067	31.555	93.671	126.936	−7.367
1000	55.517	351.952	314.869	37.084	93.851	130.623	−6.823
1100	55.907	357.263	318.485	42.656	94.022	134.292	−6.377
1200	56.222	362.141	321.922	48.263	94.184	137.946	−6.005
1300	56.480	366.652	325.192	53.898	94.336	141.586	−5.689
1400	56.692	370.845	328.305	59.557	94.477	145.215	−5.418
1500	56.869	374.763	331.273	65.235	94.605	148.835	−5.183
1600	57.017	378.438	334.107	70.930	94.717	152.446	−4.977
1700	57.142	381.899	336.817	76.638	94.813	156.051	−4.795
1800	57.249	385.168	339.414	82.358	94.890	159.651	−4.633
1900	57.341	388.266	341.904	88.087	94.946	163.247	−4.488
2000	57.421	391.209	344.296	93.825	94.979	166.841	−4.357
2100	57.490	394.012	346.597	99.571	94.987	170.434	−4.239
2200	57.550	396.688	348.814	105.323	94.959	174.028	−4.132
2300	57.603	399.247	350.951	111.081	94.923	177.622	−4.034
2400	57.650	401.700	353.015	116.843	94.849	181.219	−3.944
2500	57.692	404.054	355.010	122.611	94.746	184.820	−3.862
2600	57.729	406.318	356.940	128.382	94.614	188.425	−3.786
2700	57.763	408.497	358.810	134.156	94.454	192.036	−3.715
2800	57.792	410.598	360.622	139.934	94.256	195.654	−3.650
2900	57.819	412.627	362.380	145.715	94.050	199.278	−3.589
3000	57.844	414.587	364.088	151.498	93.809	202.911	−3.533
3100	57.866	416.484	365.748	157.283	93.543	206.553	−3.480
3200	57.886	418.322	367.362	163.071	93.254	210.202	−3.431
3300	57.905	420.104	368.934	168.861	92.944	213.861	−3.385
3400	57.922	421.832	370.464	174.652	92.614	217.531	−3.342
3500	57.937	423.512	371.956	180.445	92.257	221.209	−3.301
3600	57.951	425.144	373.411	186.239	91.905	224.899	−3.263
3700	57.965	426.732	374.831	192.035	91.528	228.598	−3.227
3800	57.977	428.278	376.217	197.832	91.139	232.308	−3.193
3900	57.988	429.784	377.571	203.630	90.740	236.028	−3.161
4000	57.998	431.252	378.895	209.430	90.331	239.759	−3.131
4100	58.008	432.685	380.189	215.230	89.915	243.499	−3.102
4200	58.017	434.083	381.456	221.031	89.493	247.250	−3.075
4300	58.025	435.448	382.696	226.833	89.065	251.012	−3.049
4400	58.033	436.782	383.910	232.636	88.633	254.783	−3.025
4500	58.040	438.086	385.099	238.440	88.197	258.563	−3.001
4600	58.047	439.362	386.265	244.244	87.759	262.354	−2.979
4700	58.054	440.610	387.408	250.049	87.317	266.154	−2.958
4800	58.060	441.833	388.529	255.855	86.874	269.964	−2.938
4900	58.065	443.030	389.630	261.661	86.428	273.784	−2.919
5000	58.071	444.203	390.709	267.468	85.979	277.612	−2.900
5100	58.076	445.353	391.769	273.276	85.529	281.449	−2.883
5200	58.081	446.481	392.811	279.083	85.075	285.294	−2.866
5300	58.085	447.587	393.834	284.892	84.618	289.150	−2.850
5400	58.089	448.673	394.839	290.700	84.157	293.013	−2.834
5500	58.093	449.739	395.828	296.510	83.692	296.884	−2.820
5600	58.097	450.786	396.800	302.319	83.220	300.766	−2.805
5700	58.101	451.814	397.756	308.129	82.743	304.654	−2.792
5800	58.104	452.824	398.697	313.939	82.258	308.552	−2.779
5900	58.107	453.818	399.623	319.750	81.754	312.457	−2.766
6000	58.111	454.794	400.534	325.561	81.250	316.372	−2.754

PREVIOUS: CURRENT: March 1996 (1 bar)

Bromine Oxide (BrO_3) **Ideal Gas** $M_r = 127.9022$

$\Delta_{at}H°(298.15\ K) = [625 \pm 50]\ kJ{\cdot}mol^{-1}$
$S°(298.15\ K) = [284.5 \pm 2]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = [233 \pm 50]\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = [221 \pm 50]\ kJ{\cdot}mol^{-1}$

Electronic Level and Quantum Weight		
state	ϵ_i, cm^{-1}	g_i
$[^2A_1]$	0.0	[2]

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[442](1)
[800](1)
[350](2)
[828](2)

Point Group: C_{3v} $\sigma = 3$
Bond Distance: Br–O = [1.68]Å
Bond Angle: O–Br–O = [89]°
Product of the Moments of Inertia: $I_A I_B I_C = 2198.7927 \times 10^{-117}$ g^{3}cm^6

Enthalpy of Formation

We adopt an enthalpy of formation value which is based on an assumed relationship of $\Delta_{at}H°(BrO_3,g)/3 = 0.9D_0^{\circ}(BrO)$.

An enthalpy of formation value (at 298.15 K) has been reported by Farkas and Klein.[1] This value, 23 kcal·mol^{-1} (96 kJ·mol^{-1}), was derived from absorption spectra measurements of bromate ions in solutions. There is considerable uncertainty in this value, both in terms of the experimental measurements and the fact that the authors have interchanged BrO_3 and BrO_3^-. This corresponds to an average bond energy of 254 kJ·mol^{-1}. In comparison $D_0^{\circ}(BrO) = 231$ kJ·mol^{-1}.

Heat Capacity and Entropy

The structure of this molecule is estimated to be pyramidal with a O–Br–O angle of [89]° and a bond length of [1.68] Å, in analogy with the corresponding chlorine and iodine oxide molecules. Venkateswarlu and Sundaram,[2] Venkateswarlu and Rajalakshmi,[3] Rao and Santhamma,[4] Rao,[5] and Thirugnanasambandam and Mohan[6] assumed the same structure and bond angle for ClO_3, BrO_3, and IO_3. Using Badgers' rule, the authors examined the relationship between the vibrational frequencies and force constants for the three pyramidal molecules – ClO_3, BrO_3, and IO_3. Although these authors refer to early measurements of the vibrational frequencies, the values appear to be in part, those of the ion BrO_3^-. The vibrational frequencies are derived from the force constants which describe the other halogen oxide molecules. The principal moments of inertia (in g cm^2) are: $I_A = 12.2156 \times 10^{-39}$, $I_B = 12.2156 \times 10^{-39}$, and $I_C = 14.7352 \times 10^{-39}$.

Byberg,[7] in an EPR study, suggested the molecule had C_{3v} symmetry with a bond angle of 112° and bond length of 1.57 Å. In contrast, Begum *et al.*,[8] in a radiolysis study, suggested a bond length of 114° with C_{3v} symmetry. In calculating atomic phase shifts, Lee and Beni[9] calculated a bond length of 1.66 Å in solution. In these cases, there is no definitive evidence as to the geometry. Values were suggested which would be consistent with experimental observations.

References

[1] L. Farkas and F. S. Klein, J. Chem. Phys. **16**(9), 886–93 (1948).
[2] K. Venkateswarlu and S. Sundaram, Proc. Phys. Soc. (London) **A69**, 180 (1956).
[3] K. Venkateswarlu and K. V. Rajalakshmi, Indian J. Pure Appl. Phys. **1**, 330 (1963).
[4] C. G. R. Rao and C. Santhamma, Current Sci. **33**(22), 677 (1964).
[5] C. G. R. Rao, Sci. Cult. **38**(12), 522 (1972).
[6] P. Thirugnanasambandam and S. Mohan, Indian J. Phys. **52B**(3), 173 (1978).
[7] J. R. Byberg, J. Chem. Phys. **83**(3), 919 (1985).
[8] A. Begum, S. Subramanuan, and M. C. R. Symons, J. Chem. Soc. **6**, 918 (1970).

Bromine oxide (BrO_3) **$Br_1O_3(g)$**

Enthalpy Reference Temperature = T_r = 298.15 K; Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	C_p°	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	.000	INFINITE	−13.101	233.000	233.000	INFINITE
50	33.333	209.520	438.271	−11.438	232.073	233.759	−244.206
100	36.646	233.329	330.438	−9.711	230.636	235.992	−123.269
150	43.085	249.376	300.850	−7.721	229.279	238.971	−83.217
200	49.535	262.667	289.684	−5.403	228.126	242.381	−63.303
250	55.297	274.354	285.471	−2.779	227.156	246.060	−51.411
298.15	59.999	284.509	284.509	.000	220.821	250.432	−43.875
300	60.162	284.880	284.510	.111	220.781	250.616	−43.636
400	67.300	303.241	286.965	6.511	205.483	263.728	−34.439
500	71.849	318.785	291.815	13.485	206.024	278.233	−29.067
600	74.791	332.164	297.452	20.827	206.767	292.607	−25.474
700	76.759	343.850	303.263	28.411	207.599	306.849	−22.897
800	78.125	354.194	308.995	36.159	208.466	320.969	−20.957
900	79.105	363.456	314.541	44.023	209.340	334.979	−19.442
1000	79.829	371.830	319.858	51.972	210.208	348.892	−18.224
1100	80.377	379.465	324.935	59.983	211.065	362.719	−17.224
1200	80.801	386.478	329.775	68.043	211.905	376.469	−16.387
1300	81.136	392.959	334.389	76.140	212.728	390.149	−15.676
1400	81.404	398.982	338.791	84.268	213.530	403.767	−15.065
1500	81.623	404.606	342.993	92.420	214.311	417.327	−14.533
1600	81.803	409.880	347.010	100.591	215.067	430.837	−14.065
1700	81.953	414.844	350.856	108.779	215.797	444.300	−13.652
1800	82.080	419.532	354.542	116.981	216.498	457.721	−13.283
1900	82.187	423.972	358.080	125.195	217.168	471.104	−12.952
2000	82.279	428.190	361.481	133.418	217.805	484.452	−12.653
2100	82.358	432.207	364.754	141.650	218.406	497.770	−12.381
2200	82.428	436.040	367.908	149.889	218.971	511.060	−12.134
2300	82.488	439.705	370.951	158.135	219.499	524.324	−11.908
2400	82.541	443.217	373.889	166.387	219.987	537.566	−11.700
2500	82.588	446.587	376.730	174.643	220.436	550.790	−11.508
2600	82.630	449.827	379.480	182.904	220.846	563.996	−11.331
2700	82.667	452.947	382.143	191.169	221.217	577.187	−11.166
2800	82.700	455.954	384.726	199.437	221.551	590.365	−11.013
2900	82.730	458.856	387.232	207.709	221.847	603.531	−10.871
3000	82.757	461.661	389.667	215.983	222.108	616.688	−10.737
3100	82.781	464.375	392.033	224.260	222.336	629.838	−10.613
3200	82.804	467.004	394.335	232.539	222.532	642.979	−10.496
3300	82.824	469.552	396.576	240.821	222.698	656.115	−10.385
3400	82.843	472.025	398.759	249.104	222.837	669.247	−10.282
3500	82.859	474.427	400.887	257.389	222.950	682.374	−10.184
3600	82.875	476.761	402.962	265.676	223.040	695.500	−10.091
3700	82.889	479.032	404.988	273.964	223.109	708.622	−10.004
3800	82.903	481.243	406.965	282.254	223.158	721.745	−9.921
3900	82.915	483.396	408.898	290.545	223.190	734.865	−9.842
4000	82.926	485.496	410.786	298.837	223.207	747.984	−9.768
4100	82.937	487.543	412.634	307.130	223.209	761.104	−9.697
4200	82.946	489.542	414.441	315.424	223.199	774.223	−9.629
4300	82.956	491.494	416.210	323.719	223.178	787.343	−9.564
4400	82.964	493.401	417.943	332.015	223.145	800.463	−9.503
4500	82.972	495.266	419.641	340.312	223.104	813.584	−9.444
4600	82.979	497.089	421.305	348.609	223.053	826.706	−9.388
4700	82.986	498.874	422.936	356.908	222.994	839.830	−9.334
4800	82.993	500.621	424.537	365.207	222.926	852.955	−9.282
4900	82.999	502.333	426.107	373.506	222.849	866.082	−9.233
5000	83.005	504.009	427.648	381.807	222.764	879.210	−9.185
5100	83.010	505.653	429.162	390.107	222.670	892.340	−9.139
5200	83.015	507.265	430.648	398.409	222.565	905.471	−9.096
5300	83.020	508.846	432.109	406.710	222.451	918.606	−9.053
5400	83.025	510.398	433.544	415.013	222.324	931.741	−9.013
5500	83.029	511.922	434.955	423.315	222.185	944.879	−8.974
5600	83.033	513.418	436.343	431.618	222.032	958.022	−8.936
5700	83.037	514.888	437.708	439.922	221.863	971.165	−8.900
5800	83.041	516.332	439.052	448.226	221.678	984.313	−8.865
5900	83.044	517.751	440.373	456.530	221.474	997.462	−8.831
6000	83.048	519.147	441.675	464.835	221.250	1010.617	−8.798

PREVIOUS: CURRENT: March 1996 (1 bar)

$\Delta_{at}H°(0\ K) = 358 \pm 5\ kJ \cdot mol^{-1}$
$S°(298.15\ K) = 290.8 \pm 2\ J\ K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 124.1 \pm 3.5\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 107.6 \pm 3.5\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
state	ϵ_i, cm^{-1}	g_i
X^1A	0.0	1

Vibrational Frequencies and Degeneracies ν, cm^{-1}
526.1 (1)
180 (1)
623.4 (1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: Br–O = 1.8429 Å
Bond Angle: Br–O–Br = 112.24°
Product of the Moments of Inertia: $I_A I_B I_C = 10238.8084 \times 10^{-117}\ g^3cm^6$

Enthalpy of Formation

Thorn *et al.*[3] using experimental results from photoionization efficiency spectrum of Br_2O, along with the ionization and appearance energy, have derived a value of the enthalpy of formation $\Delta_f H(Br_2O, 0\ K) = 124.1 \pm 3.5\ kJ \cdot mol^{-1}$, which we adopt.

There are three other related studies leading to an enthalpy of formation. Orlando and Burkholder[1] measured the equilibrium constant for the reaction: $Br_2O + H_2O = 2HOBr$. They determined $\Delta_r G°(298\ K) = 9.70\ kJ \cdot mol^{-1}$. Using the thermal functions presented in this table and thermal functions for HOBr(g) given by JANAF,[2] we calculate $\Delta_f H°(Br_2O, g, 298.15) = 107.6 \pm 3.5\ kJ \cdot mol^{-1}$. This value supports our adopted value. Assuming that the values $D_0°(ClO)$ and $\Delta_{at}H°(OClO, g)$ are reasonable, we would anticipate the ratio of the numbers (1.52) to apply for a similar relationship between BrO(g) and BrOBr(g). This would yield a value of 114 $kJ \cdot mol^{-1}$ which is in good agreement with our adopted value. Using the estimation scheme of Novak[4] (in part based on ab initio calculations and an extended basis set), the enthalpy of formation was calculated to be 83 ± 8 $kJ \cdot mol^{-1}$ at 0 K.

Heat Capacity and Entropy

Mueller and Cohen,[5] from the microwave spectra of three isotopomers of BrOBr(g), have determined $r_0 = 1.8429$ Å and <(BrOBr) = 112.24°, which we adopt. Supporting evidence was derived from bromine K–edge EXAFS study of Levason *et al.*[6] The structure of this molecule was bent with a Br–O–Br angle of 112 ± 2° and the Br–O bond length was 1.85 ± 0.01 Å. The bond angle is in good agreement with the value derived from matrix IR studies[7] where a value of 113° was estimated from isotope shifts. In comparison, Novak,[4] with the aid of ab initio calculations, determined a bond length of 1.809 Å and a bond angle of 115.7°. The principal moments of inertia (in g cm^2) are: $I_A = 2.5488 \times 10^{-39}$, $I_B = 62.1189 \times 10^{-39}$, and $I_C = 64.6677 \times 10^{-39}$.

The recommended vibrational frequencies (ν_1, ν_3) are those suggested by Jacox.[8] These results are based on the infrared spectra of the argon matrix isolated radical as studied by Tevault *et al.*,[9] Allen *et al.*,[7] and Levason *et al.*[6] A value of $\nu_2 = 197\ cm^{-1}$ reported in the solid IR spectra study of Campbell *et al.*[10] However, the Mueller and Cohen[5] study implied $\nu_2 = 180\ cm^{-1}$ (± 5). Lee,[11] using ab initio calculations – CCSD(T) – derived vibrational frequencies (513, 180 and 613 cm^{-1}) which are in reasonable agreement with our adopted values. Similar calculations by Lee yielded a structure in agreement with our recommendations (112.9° and 1.865 Å).

All specific studies (condensed or matrix)[5-12] yielded values for ν_1 and ν_3 which are in reasonable agreement. Although Tevault *et al.*[9] stated that the values for ν_1 and ν_3 reported by Campbell *et al.*[10] are reversed, this does not affect the thermal functions.

Anthar and Dostrovsky[13] measured the ultraviolet absorption spectra of Br_2O in CCl_4. A strong absorption band was observed at 2800 Å (35714 cm^{-1}). We assume this refers to the position of the first excited electronic state. This state is not included in the calculations.

References

[1]J. J. Orlando and J. B. Burkholder, J. Phys. Chem. **99**, 1143–50 (1995).
[2]JANAF Thermochemical Tables: HOBr(g), June 1995.
[3]R. P. Thorn Jr., P. S. Monks, L. J. Stief, S.–C. Kuo, Z. Zhang and R. B. Klemm, Brookhaven National Laboratory, BNL #62126, 11pp. (1995); J. Phys. Chem. (1996, in press).
[4]I. Novak, Struct. Chem. **3**(6), 377–9 (1992).
[5]H. S. P. Mueller and E. A. Cohen, submitted for publication in J. Phys. Chem.
[6]W. Levason, J. S. Ogden, M. D. Spicer, and N. A. Young, J. Am. Chem. Soc. **112**, 1019 (1990).
[7]D. Allen, M. Poliakoff, and J. J. Turner, J. Mol. Struct. **157**, 1 (1987).
[8]M. E. Jacox, J. Phys. Chem. Ref. Data, Monograph No. 3, 461 pp. (1994).
[9]D. E. Tevault, N. Walker, R. R. Smardzewski, and W. B. Fox, J. Phys. Chem. **82**, 2733 (1978).
[10]C. Campbell, J. P. M. Jones, and J. J. Turner, Chem. Commun. (**15**), 888 (1968).
[11]T. J. Lee, J. Phys. Chem. **99**, 15074–80 (1995).
[12]J. L. Pascal, A. C. Pavia, J. Potier, and A. Potier, Proc. Int. Conf. Raman Spectrosc. 5th (1976), No. 210447, 120–1 (pub. 1977).

Enthalpy Reference Temperature = T_r = 298.15 K; Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_f H°$ (kJ·mol⁻¹)	$\Delta_f G°$ (kJ·mol⁻¹)	log K_f
0	.000	.000	INFINITE	−12.399	124.100	124.100	INFINITE
50	34.529	217.773	432.252	−10.724	124.219	118.511	−123.808
100	38.480	242.978	331.921	−8.894	123.359	113.112	−59.083
150	41.918	259.228	305.126	−6.885	122.314	108.209	−37.682
200	45.264	271.753	295.272	−4.704	121.193	103.675	−27.077
250	48.075	282.168	291.638	−2.367	119.985	99.433	−20.775
298.15	50.168	290.823	290.823	.000	107.648	96.902	−16.977
300	50.238	291.133	290.824	.093	107.574	96.835	−16.861
400	53.068	306.013	292.833	5.272	76.787	99.594	−13.006
500	54.685	318.044	296.711	10.667	76.961	105.277	−10.998
600	55.664	328.108	301.128	16.188	77.183	110.920	−9.656
700	56.293	336.739	305.614	21.788	77.417	116.524	−8.695
800	56.717	344.285	309.986	27.440	77.648	122.095	−7.972
900	57.016	350.984	314.176	33.127	77.869	127.637	−7.408
1000	57.234	357.003	318.163	38.840	78.077	133.156	−6.955
1100	57.397	362.466	321.946	44.572	78.271	138.654	−6.584
1200	57.523	367.466	325.534	50.318	78.451	144.135	−6.274
1300	57.621	372.074	328.939	56.076	78.616	149.602	−6.011
1400	57.700	376.347	332.174	61.842	78.766	155.057	−5.785
1500	57.763	380.330	335.254	67.615	78.900	160.501	−5.589
1600	57.816	384.060	338.189	73.394	79.016	165.938	−5.417
1700	57.859	387.566	340.991	79.178	79.113	171.367	−5.265
1800	57.896	390.875	343.671	84.966	79.189	176.791	−5.130
1900	57.927	394.006	346.239	90.757	79.242	182.212	−5.009
2000	57.953	396.978	348.702	96.551	79.269	187.631	−4.900
2100	57.976	399.806	351.069	102.347	79.269	193.049	−4.802
2200	57.996	402.503	353.346	108.146	79.239	198.468	−4.712
2300	58.014	405.082	355.540	113.947	79.179	203.889	−4.630
2400	58.029	407.551	357.656	119.749	79.087	209.313	−4.556
2500	58.042	409.920	359.699	125.552	78.963	214.741	−4.487
2600	58.054	412.197	361.675	131.357	78.807	220.175	−4.423
2700	58.065	414.388	363.587	137.163	78.618	225.616	−4.365
2800	58.074	416.500	365.439	142.970	78.400	231.064	−4.311
2900	58.083	418.538	367.235	148.778	78.152	236.521	−4.260
3000	58.091	420.507	368.978	154.587	77.877	241.986	−4.213
3100	58.098	422.412	370.671	160.396	77.577	247.462	−4.170
3200	58.104	424.257	372.317	166.206	77.254	252.947	−4.129
3300	58.110	426.045	373.918	172.017	76.912	258.442	−4.091
3400	58.115	427.780	375.477	177.828	76.554	263.949	−4.055
3500	58.120	429.464	376.996	183.640	76.181	269.465	−4.022
3600	58.125	431.102	378.476	189.452	75.798	274.994	−3.990
3700	58.129	432.694	379.920	195.265	75.407	280.532	−3.960
3800	58.132	434.245	381.329	201.078	75.011	286.081	−3.932
3900	58.136	435.755	382.706	206.891	74.612	291.641	−3.906
4000	58.139	437.227	384.050	212.705	74.214	297.211	−3.881
4100	58.142	438.662	385.365	218.519	73.818	302.791	−3.858
4200	58.145	440.063	386.651	224.334	73.427	308.380	−3.835
4300	58.148	441.432	387.909	230.148	73.042	313.979	−3.814
4400	58.150	442.768	389.140	235.963	72.666	319.586	−3.794
4500	58.152	444.075	390.347	241.778	72.299	325.202	−3.775
4600	58.154	445.353	391.529	247.593	71.944	330.826	−3.757
4700	58.156	446.604	392.687	253.409	71.600	336.458	−3.739
4800	58.158	447.828	393.823	259.225	71.270	342.097	−3.723
4900	58.160	449.028	394.938	265.041	70.953	347.743	−3.707
5000	58.162	450.203	396.031	270.857	70.650	353.395	−3.692
5100	58.163	451.354	397.105	276.673	70.362	359.053	−3.677
5200	58.165	452.484	398.159	282.489	70.088	364.715	−3.664
5300	58.166	453.592	399.194	288.306	69.829	370.384	−3.650
5400	58.167	454.679	400.212	294.123	69.583	376.057	−3.638
5500	58.169	455.746	401.212	299.939	69.352	381.734	−3.625
5600	58.170	456.794	402.195	305.756	69.134	387.416	−3.614
5700	58.171	457.824	403.162	311.573	68.930	393.102	−3.602
5800	58.172	458.836	404.113	317.390	68.738	398.791	−3.591
5900	58.173	459.830	405.049	323.208	68.557	404.482	−3.581
6000	58.174	460.808	405.970	329.025	68.388	410.178	−3.571

PREVIOUS: CURRENT: March 1996 (1 bar)

Bromine Oxide (BrBrO) | Ideal Gas | $M_r = 175.8074$

$S°(298.15 K) = [312.7 \pm 2]$ J K^{-1}·mol^{-1}

$\Delta_f H°(0 K) = [183.7 \pm 20]$ kJ·mol^{-1}
$\Delta_f H°(298.15 K) = [168 \pm 20]$ kJ·mol^{-1}

Electronic Level and Quantum Weight		
state	ϵ_i, cm^{-1}	g_i
$[^1A'']$	0.0	[3]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
804 (1)
[150] (1)
236 (1)

Point Group: C_s $\sigma = 1$
Bond Distances: Br–O = [1.69] Å; Br–Br = [2.51] Å
Bond Angle: Br–Br–O = [113.1]°
Product of the Moments of Inertia: $I_A I_B I_C = [13784.9110 \times 10^{-117}]$ g^{3}cm^6

Enthalpy of Formation

For the four halogen oxide species, XXO(g) where X = F, Cl, Br, I, there is no experimental data related to the enthalpy of formation. Lee[1] determined the enthalpies of formation of many triatomic bromine compounds using a combination of theoretical isomeric, homodesmic and isodesmic reaction energies. The calculated results suggested that BrBrO is less stable than BrOBr by 14.6 kcal·mol^{-1} (61.1 kJ·mol) at 298.15 K.

Heat Capacity and Entropy

Lee,[1] using ab initio calculations – CCSD(T) – derived a bond angle of 113.1° and bond distances r(Br–Br) = 2.510 Å and r(Br–O) = 1.690 Å, which we adopt. The principal moments of inertia (in g cm^2) are: $I_A = 4.7079 \times 10^{-39}$, $I_B = 51.8084 \times 10^{-39}$, and $I_C = 56.5163 \times 10^{-39}$.

The recommended vibrational frequencies are those suggested by Jacox.[2] These results are based on the infrared spectra of the argon matrix isolated radical as studied by Tevault *et al.*[3] ν_2 is estimated based on comparisons of the vibrational frequencies with ClOO. Lee,[1] using ab initio calculations, derived the vibrational frequencies to be 793, 153 and 215 cm^{-1}. These are in excellent agreement with our recommendations.

Tevault *et al.*[3] observed very intense bands at 804 and 236 cm^{-1} which appeared when Ar–Br_2–O_3 matrices were photolyzed with 632.8 nm light. The assignments for BrBrO were assumed to be ν_1 = 804 cm^{-1} (Br–O stretch), ν_3 = 236 cm^{-1} (Br–Br stretch) and the ν_2 value (the bending mode) was expected to be below 200 cm^{-1}.

References

[1] T. J. Lee, J. Phys. Chem. **99**, 15074–80 (1995).
[2] M. E. Jacox, J. Phys. Chem. Ref. Data, Monograph No. 3, 461 pp. (1994).
[3] D. E. Tevault, N. Walker, R. R. Smardzewski, and W. B. Fox, J. Phys. Chem. **82**, 2733 (1978).

Bromine oxide (BrBrO) Br_2O_1(g)

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	-13.138	183.713	183.713	INFINITE
50	35.814	234.286	463.229	-11.447	183.848	177.315	-185.239
100	42.429	261.298	356.090	-9.479	183.126	171.047	-89.346
150	46.014	279.255	327.647	-7.259	182.292	165.183	-57.522
200	48.247	292.815	317.312	-4.899	181.349	159.619	-41.688
250	49.997	303.775	313.543	-2.442	180.262	154.309	-32.241
298.15	51.385	312.704	312.704	.000	168.000	150.730	-26.407
300	51.433	313.022	312.705	.095	167.928	150.623	-26.226
400	53.530	328.128	314.750	5.351	137.218	151.179	-19.742
500	54.868	340.228	318.676	10.776	137.422	154.646	-16.156
600	55.735	350.313	323.132	16.309	137.656	158.069	-13.761
700	56.316	358.951	327.647	21.913	137.895	161.453	-12.048
800	56.719	366.499	332.041	27.566	138.127	164.802	-10.760
900	57.008	373.197	336.249	33.253	138.347	168.123	-9.758
1000	57.222	379.215	340.250	38.965	138.554	171.420	-8.954
1100	57.384	384.677	344.044	44.696	138.747	174.698	-8.296
1200	57.509	389.676	347.642	50.441	138.925	177.958	-7.746
1300	57.608	394.283	351.054	56.197	139.089	181.204	-7.281
1400	57.687	398.555	354.297	61.962	139.238	184.438	-6.881
1500	57.752	402.537	357.381	67.734	139.371	187.662	-6.535
1600	57.805	406.266	360.321	73.512	139.486	190.877	-6.231
1700	57.849	409.772	363.128	79.295	139.582	194.086	-5.964
1800	57.887	413.080	365.812	85.081	139.657	197.290	-5.725
1900	57.918	416.210	368.383	90.872	139.708	200.490	-5.512
2000	57.946	419.182	370.849	96.665	139.735	203.689	-5.320
2100	57.969	422.010	373.219	102.461	139.734	206.886	-5.146
2200	57.989	424.707	375.498	108.259	139.704	210.085	-4.988
2300	58.007	427.285	377.694	114.059	139.643	213.285	-4.844
2400	58.023	429.754	379.812	119.860	139.550	216.488	-4.712
2500	58.037	432.123	381.858	125.663	139.426	219.697	-4.590
2600	58.049	434.400	383.835	131.467	139.269	222.910	-4.478
2700	58.060	436.591	385.749	137.273	139.080	226.131	-4.375
2800	58.070	438.702	387.602	143.079	138.861	229.359	-4.279
2900	58.079	440.740	389.400	148.887	138.613	232.595	-4.189
3000	58.087	442.709	391.144	154.695	138.337	235.841	-4.106
3100	58.094	444.614	392.838	160.504	138.037	239.096	-4.029
3200	58.101	446.459	394.485	166.314	137.714	242.361	-3.956
3300	58.107	448.246	396.088	172.124	137.372	245.636	-3.888
3400	58.112	449.981	397.647	177.935	137.013	248.922	-3.824
3500	58.117	451.666	399.167	183.747	136.640	252.219	-3.764
3600	58.122	453.303	400.648	189.559	136.256	255.527	-3.708
3700	58.126	454.896	402.093	195.371	135.865	258.845	-3.654
3800	58.130	456.446	403.503	201.184	135.469	262.175	-3.604
3900	58.134	457.956	404.880	206.997	135.070	265.514	-3.556
4000	58.137	459.428	406.225	212.811	134.671	268.864	-3.511
4100	58.140	460.863	407.540	218.624	134.275	272.224	-3.468
4200	58.143	462.264	408.827	224.438	133.884	275.593	-3.427
4300	58.146	463.632	410.085	230.253	133.499	278.972	-3.389
4400	58.148	464.969	411.318	236.068	133.122	282.359	-3.352
4500	58.150	466.276	412.524	241.883	132.756	285.755	-3.317
4600	58.153	467.554	413.707	247.698	132.400	289.158	-3.283
4700	58.155	468.805	414.866	253.513	132.056	292.570	-3.252
4800	58.157	470.029	416.002	259.329	131.726	295.989	-3.221
4900	58.158	471.228	417.117	265.144	131.409	299.415	-3.192
5000	58.160	472.403	418.211	270.960	131.106	302.846	-3.164
5100	58.162	473.555	419.285	276.776	130.817	306.284	-3.137
5200	58.163	474.684	420.340	282.593	130.543	309.727	-3.111
5300	58.165	475.792	421.376	288.409	130.284	313.176	-3.087
5400	58.166	476.880	422.393	294.226	130.038	316.629	-3.063
5500	58.167	477.947	423.394	300.042	129.807	320.086	-3.040
5600	58.168	478.995	424.377	305.859	129.589	323.548	-3.018
5700	58.170	480.025	425.345	311.676	129.384	327.013	-2.997
5800	58.171	481.036	426.296	317.493	129.192	330.482	-2.976
5900	58.172	482.031	427.232	323.310	129.012	333.954	-2.957
6000	58.173	483.008	428.154	329.127	128.842	337.429	-2.938

PREVIOUS: CURRENT: March 1996 (1 bar)

Bromine oxide (BrBrO) Br_2O_1(g)

7. Conclusions

Of the bromine oxides mentioned in the literature, only nine have been prepared (as a single crystal, or in the gas phase, or a matrix) and (at least, partially) characterized: BrO, BrBrO, BrOBr, OBrO, BrOO, Br_2O_3, O_2BrBrO_2, $O_2BrOBrO$, and Br_2O_5. Only early studies exist which mention Br_2O_6 and Br_2O_7; it would appear that these species do not exist. BrO_3 and BrO_4 are proposed as intermediates in solutions or crystalline environments, with only an absorption maximum as a characterization.

Early references to Br_3O_8 are undoubtedly incorrect. Difficulties in the experimental determination of the true identity and composition of the solid oxides caused difficulty for all the condensed bromine oxides in the period before 1970. Recent references to this oxide are also incorrect in the sense that they should have been indexed to the monoxide—BrO. Thus, at this time, there is considerable uncertainly as to the existence of this compound. Finally, even recent evidence suggests that the characterization of the various isomers of Br_2O_4 may not be correct.

In the following table, a summary of the recommended thermodynamic properties at ambient conditions for six bromine oxides are given. The brackets indicate estimated values. The recommended values contain significant uncertainties. In all cases, experimental enthalpy of formation data are needed. However, due to its importance in atmospheric chemistry, the prime effort should be directed at determining experimentally the enthalpy of formation of OBrO(g). Further efforts should be directed towards confirming the dissociation energy of BrO and the enthalpy of formation of BrOBr(g), and establishing the enthalpies of formation for BrOO(g), BrBrO(g) and BrO_3(g). For any of the polyatomic gaseous species, except BrOBr, spectroscopic measurements for the geometry and vibrational frequencies would greatly reduce the uncertainties in the resulting thermal functions. Confirmation as to the existence of the various condensed phases is needed, although this is a much lower priority. Heat capacity and enthalpy are not necessary at this time. (See Table 7.1.)

TABLE 7.1. Thermodynamic Properties of the Bromine Oxides.

	0 K	298.15 K			
	$\Delta_f H^0$	$\Delta_f H^0$	$\Delta_f G^0$	C_p^0	S^0
Compound		kJ mol^{-1}		J mol^{-1} K^{-1}	
BrO(g)	133.3±2.4	125.8±2.4	109.6	34.2	232.97±0.1
OBrO(g)	[161.5±25]	[152.0±25]	[155.0]	45.4	271.1±2
BrOO(g)	[116.1±40]	[108.0±40]	[105.7]	[48.9]	[288.8±3]
BrO_3(g)	[233±50]	[221±50]	[250.4]	[60]	[284.5±2]
BrOBr(g)	124.1±3.5	107.6±3.5	96.9	50.2	290.8±2
BrBrO(g)	[183.7±20]	[168±20]	[150.7]	[51.4]	[312.7±2]

8. Acknowledgments

This work was undertaken as part of a larger study to provide NIST–JANAF Thermochemical Tables for as many halogen oxide species as possible. This particular study for the bromine oxides was supported by the Standard Reference Data Program at the U.S. National Institute of Standards and Technology. The author is particularly grateful for the help of Sabina Crisen who confirmed the completeness of the annotated bibliographies, created the numerous tables which summarize the reported experimental studies, and obtained copies of the pertinent articles. In addition to the anonymous reviewers of this article, the contribution of Stanley Abramowitz in discussions on the spectroscopic properties of the triatomic molecules is greatly appreciated; Edward A. Cohen (JPL) for providing data prior to publication and for reviewing portions of this article; Holger Mueller (JPL) for reviewing portions of this article; and R. B. Klemm (Brookhaven National Lab) for information pertaining to the enthalpy of formation of Br_2O as well as reviewing this article. The BrO calculations were performed by David Neumann.

9. References—Annotated Bibliographies

The following articles are a combination of all references dealing with the bromine oxides. Where possible, we have tried to include all authors, title, journal, a citation to Chemical Abstracts, and an annotation indicating the type of study. In general, dissertations (especially non-US) have not been obtained and read.

28LEW/SCH B. Lewis and H.-J. Schumacher, "The existence of an oxide of bromine," Z. Phys. Chem., Abt. A **138**, 462 (1928); CA 23 3416(7); preparation.

29LEW/SCH B. Lewis and H.-J. Schumacher, "Preparation and properties of a bromine oxide," Z. Anorg. Allgem. Chem. **182**, 182–6 (1929); CA 23 5426(3); preparation, decomposition.

29LEW/SCH2 B. Lewis and H.-J. Schumacher, "Thermal reaction between bromine and ozone," Z. Elektrochem. **35**, 648–52 (1929); CA 24 2033(8); preparation.

30BRA W. C. Bray, "An oxide of iodine, I_2O_2. An intermediate compound," J. Am. Chem. Soc. **52**, 3580–6 (1930); CA 24 5654; in aqueous solution.

30LEW/SCH B. Lewis and H.-J. Schumacher, "A first order solid phase reaction," Nature **125**, 129 (1930); CA 24 2033(8); kinetics.

30ZIN/RIE E. Zintl and G. Rienacker, "Existence of a volatile bromine oxide," Ber. **63B**, 1098–1104 (1930); CA 24 5249(3); preparation.

31LEW/FEI B. Lewis and W. Feitknecht, "The kinetics of gas explosions: the thermal decomposition of ozone sensitized by bromine vapor," J. Am. Chem. Soc. **53**, 2910–34 (1931); decomposition of ozone.

31SPI J. W. T. Spinks, "Photosensitized decomposition of ozone by bromine," Nature **128**, 548 (1931); decomposition of ozone.

34BRA O. L. Brady, "Recent advances in science: general and organic chemistry," Sci. Prog. **29**, 101–9 (1934); CA 28 6598(8); review.

34SKR A. Skrabal, "Reactions of alkaline halogen bleaches [hypohalites]," Z. Elektrochem. Angew. Phys. Chem. **40**, 232–46 (1934); CA 28 4997(1); re-examination of available data in aqueous solution.

35BRE/SCH W. Brenschede and H. J. Schumacher, "Bromine oxide, Br_2O," Z. Phys. Chem. B**29**, 356–8 (1935); CA 30 37(3); preparation, decomposition.

36BRE/SCH W. Brenschede and H. J. Schumacher, "The preparation and a few properties of bromine oxide of the formula Br_2O," Z. Anorg. Allgem. Chem. **226**, 370–84 (1936); CA 30 4419(7); preparation, properties.

36RAB/WOO E. Rabinowitch and W. C. Wood, "Kinetics of recombination of bromine atoms. II," Trans. Faraday Soc. **32**, 907–17 (1936); CA 30 5862(2); dissociation of Br_2 in the presence of O_2.

37SCH/SCH R. Schwarz and M. Schmeisser, "A new oxide of bromine of the formula BrO_2. I," Ber. **70B**, 1163–6 (1937); CA 31 6125(6); formation, decomposition.

37VAI W. M. Vaidya, "Flame spectra of some aliphatic halides. I. Methyl iodide," Proc. Indian Acad. Sci. **6A**, 122–8 (1937); CA 32 50(8); spectra.

38SCH/WIE R. Schwarz and H. Wiele, "The bromine oxide, Br_2O," Naturwissenschaften **26**, 742 (1938); CA 33 2430(9); preparation.

38VAI W. M. Vaidya, "Flame spectra of some aliphatic halides. II. Ethylbromide," Proc. Indian Acad. Sci. **7a**, 321–6 (1938); CA 32 6550(7); spectra.

39SCH/JAB P. W. Schenk and H. Jablonowski, "Reactions between atoms at low temperatures," Z. Anorg. Allgem. Chem. **244**, 397 (1940); Z. Elektrochem. 45, 650 (1939); preparation.

39SCH/WIE R. Schwarz and H. Wiele, "The bromine oxides. II," J. Prakt. Chem. **152**(2), 157–76 (1939); CA 33 4541(5); formation.

40MUN/SPI R. Mungen and J. W. T. Spinks, "The bromine sensitized photodecomposition of ozone," Can. J. Res. **18B**, 363–71 (1940); CA 35 692(6); formation.

47COL/GAY E. H. Coleman and A. G. Gaydon, "The radicals BrO and CBr in flames," Discussions Faraday Soc. (2), **166–9** (1947); CA 43 5312g; spectra, dissociation energy.

47KHA/BOL M. Kharasch, P. B. Bolen, and W. H Urry, "Formation of quinone by the action of bromine oxide on benzene," J. Am. Chem. Soc. **69**, 2566 (1947); CA 42 146f; reaction with benzene, toluene, and cyclohexane.

47PRA A. H. Pratt, "Esterification of cellulose," U.S. 2,429,644 (1947); CA 42 P3178h; dehydration of $HBrO_3$ to Br_2O_5, catalyst in cellulose esterification.

48FAR/KLE L. Farkas and F. S. Klein, "On the photochemistry of some ions in solution," J. Chem. Phys. **16**(9), 886–93 (1948); CA 50 16345h; enthalpy of formation.

48GAY A. G. Gaydon, *Spectroscopy and Combustion Theory*, 2nd ed. (Chapman and Hall, London, 1948), p. 92; review, dissociation energy.

50BRE/BRO L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, "Paper 6: The thermodynamic properties of the halides," *National Nuclear Energy Series 19B*, edited by L. L. Quill (McGraw-Hill, New York, 1950); dissociation energy.

50HER G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules*, 2nd ed. (Van Nostrand, Princeton, 1950); spectroscopy.

51ABE E. Abel, "Halate formation," Monatsh. Chem. **82**, 751–4 (1951); CA 46 3890g; intermediate in aqueous solution (does not specifically mention Br_2O_2).

51PFL/SCH A. Pflugmacher, R. Schwarz, and H. J. Rabbin, "Oxides of bromine. III. The heat of formation of bromine dioxide," Z. Anorg. Allgem. Chem. **264**, 204–8 (1951); CA 47 6752i; enthalpy of formation.

52EDW J. O. Edwards, "Rate laws and mechanisms of oxyanion reactions with bases," Chem. Rev. **50**, 455--82 (1952); CA 46 8482f; in aqueous solution, review.

53BRE L. Brewer, "The thermodynamic properties of the oxides and their vaporization processes," Chem. Rev. **52**, 1–66 (1953); review, dissociation energy.

53GAY A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules*, 2nd ed. (Chapman and Hall, London, 1953); dissociation energy.

53KAN N. P. Kanyaev, "Bromination of unsaturated compounds. III. Reaction of addition of hypobromous acid to allytrimethyammonium perchlorate," Sbornik Statei Obshchei Khim. **2**, 1172–7 (1953); CA 49 5087f; formation, bromination with HBrO.

53PFL A. Pflugmacher, "Bromine oxides. IV. Trinitrobromo dioxide," Z. Anorg. Allgem. Chem. **273**, 41–7 (1953); CA 48 489f; compound with NO_2, questions if the compound is not Br_2O_6.

54ANT/DOS M. Anthar and I. Dostrovsky, "Ultraviolet absorption spectra of some organic hypohalites," J. Chem. Soc. 1105–8 (1954); CA 48 6827h; spectrum in CCl_4.

54COT T. L. Cottrell, *The Strengths of Chemical Bonds* (Butterworths, London, 1954), pp. 221–81; estimated bond dissociation energy.

55PFL A. Pflugmacher, "About bromine trioxide," Angew. Chem. **67**, 524 (1955); discussion of reaction scheme.

55PFL/RAB A. Pflugmacher, H. J. Rabben, and H. Dahmen, "Bromine oxides. V. Bromine trioxide," Z. Anorg. Allgem. Chem. **279**, 313–20 (1955); CA 49 14550f; preparation, properties.

56VEN/SUN K. Venkateswarlu and S. Sundaram, ''Evaluation of force constants from Raman effect data: molecules, radicals, and groups of pyramidal XY_3 type,'' Proc. Phys. Soc. (London) A **69**, 180–3 (1956); CA 50 16345h; vibrational frequencies.

57RAM D. A. Ramsay, ''Electronic spectra of polyatomic free radicals,'' Ann. N Y Acad. Sci. **67**, 485–98 (1957); CA 51 16094a; review of electronic spectra, only passing reference to BrO (no data).

57STR/CHI R. L. Strong, J. C. W. Chien, P. E. Graf, and J. E. Willard, ''Studies of iodine atom and bromine atom recombination following flash photolysis of gaseous I_2 and Br_2,'' J. Chem. Phys. **26**, 1287–95 (1957); CA 51 13580d.

58ARV/AYM A. J. Arvia, P. J. Aymonino and H.-J. Schumacher, ''Formation of solid oxides of bromine in the thermal reaction between bromine and ozone,'' Anales Asoc. Quim. Arg. **46**, 55–65 (1958); CA 52 18048i; refer to CA 53 7849c; formation from Br and O_3.

58BRE L. Brewer, ''Dissociation energies of gaseous oxides,'' UCRL 8356, 4 pp. (1958); critical evaluation of dissociation energy.

58DUR/RAM R. A. Durie and D. A. Ramsay, ''Absorption spectra of the halogen monoxides,'' Can. J. Phys. **36**, 35–53 (1958); CA 52 4315b; absorption spectra; rotational and vibrational analysis, dissociation energy.

58MCG/NOR W. D. McGrath and R. G. W. Norrish, ''The study of energy transfer and energy distribution in fast chemical reaction by flash photolysis and kinetic spectroscopy,'' Z. Phys. Chem. (Frankfurt) **15**, 245–61 (1958); CA 52 11591f; dissociation energy.

58SIG J. Sigalla, ''Reduction of bromates by halides and the mechanism of oxidation-reduction reactions,'' J. chim. phys. **55**, 758–67 (1958); CA 53 7851a; in aqueous solution ($Br_2O_2 \cdot H_2O$).

58ZEE A. P. Zeelenberg, ''Absorption spectrum of the OBr radical,'' Nature **181**, 42 (1958); CA 52 10717c; absorption spectrum.

58ARV/AYM A. J. Arvia, P. J. Aymonino, and H. J. Schumacher, ''Formation of solid oxides of bromine in the thermal reaction between bromine and ozone,'' Anales Asoc. Quim. Arg. **46**, 55–65 (1958); Z. Anorg. Allgem. Chem. **298**, 1–8 (1959); CA 53 7849c; solid formation from bromine and ozone.

58PFL A. Pflugmacher, ''Formation of solid oxides of bromine in the thermal reaction between bromine and ozone,'' Z. Anorg. Allgem. Chem. **298**, 9–10 (1959); CA 53 7849e; response to Arvia *et al.*

59SCH/JOE M. Schmeisser and K. Joerger, ''Reactions with ozone solutions. I. Synthesis of BrO_2,'' Angew. Chem. **71**, 523–4 (1959); CA 54 5315e; preparation from Br_2 and ozone in $CFCl_3$ solutions.

59SCH H. J. Schumacher, ''Formation of solid oxides of bromine in the thermal reaction between bromine and ozone,'' Z. Anorg. Allgem. Chem. **298**, 11 (1959); CA 53 7849f; response to Pflugmacher.

60BRI/MAT N. K. Bridge and M. S. Matheson, ''The flash photolysis of halate and other ions in solution,'' J. Phys. Chem. **64**, 1280–5 (1960); CA 55 7006e; formation in hypobromate solutions.

60GEO J. W. George, ''Halides and oxyhalides of the elements of groups Vb and VIb,'' Progr. Inorg. Chem. **2**, 33–107 (1960); CA 57 10507c; review.

60MAT/DOR M. S. Matheson and L. M. Dorfman, ''Detection of short-lived transients in radiation chemistry,'' J. Chem. Phys. **32**, 1870–1 (1960); CA 55 1150c; pulse radiolysis.

61GUE/GOU H. Guenebaut and P. Goudmand, ''Molecular spectroscopy—on the excitation in shock wave, of a resulting gaseous mixture of the action of H_2SO_4 on $KBrO_3$,'' Compt. Rend. **253**, 1926–8 (1961); CA 56 15056c; shock wave, formation.

62BOY/GRA G. E. Boyd, E. W. Graham, and Q. V. Larsan, ''Recoil reactions with high intensity slow neutron sources. IV. Radiolysis of crystal alkali metal bromates with γ-rays,'' J. Phys. Chem. **66**, 300–7 (1962); CA 57 313h; radiolysis.

62GUE/PAN H. Guenbaut, G. Pannetier, and P. Goudmand, ''Excitation of gases or gas mixtures in a shock tube,'' Bull. Soc. Chim. France 1962, **80–6** (1962); CA 57 1753a; formation in reaction of H_2SO_4 and $KBrO_3$ induced by shock waves.

62SVE R. A. Svehla, ''Estimated viscosities and thermal conductivities of gases at high temperatures,'' NASA Tech. Rep. R132, 140 pp. (1962); CA 57 79c; thermal conductivity, viscosity.

63BUR/NOR G. Burns and R. G. W. Norrish, ''Mechanism of the formation of halogen monoxides during flash photolysis of halogen + oxygen mixtures,'' Proc. R. Soc. (London) A **271**, 289–95 (1963); CA 58 4076d; flash photolysis.

63SCH C. J. Schexnayder Jr., ''Tabulated values of bond dissociation energies, ionization potentials and electron affinities for some molecules found in high-temperature chemical reactions,'' NASA Tech. Note D-1791, 62 pp. (1963); dissociation energies.

63SCH/BRA M. Schmeisser and K. Brandle, ''Oxides and oxyfluorides of the halogens,'' Adv. Inorg. Chem. Radiochem. **5**, 41–89 (1963); CA 60 7657b; review.

63VEN/RAJ K. Venkateswarlu and K. V. Rajalakshmi, ''Urey-Bradley force field and thermodynamic properties: pyramidal XY_3 type molecules,'' Indian J. Pure Appl. Phys. **1**, 380–2 (1963); CA 60 4823e; vibrations.

64RAO/SAN C. G. Rama Rao and C. Santhamma, ''The mean square amplitudes of vibration in BrO_3, IO_3, and $SiBr_3$,'' Current Sci. **33**(22), 677–8 (1964); CA 62 6001e; molecular vibrations.

64TRE/YAA A. Treinin and M. Yaacobi, ''The electronic spectra of the halate ions in solution,'' J. Phys. Chem. **68**, 2487–92 (1964); CA 61 10192e; rejection of Matheson *et al.* (1960) data.

65GLU/MED V. P. Glushko and V. A. Medvedev, ''Thermal Constants of Substances,'' Volume I (145 pp.), Academy of Sciences, Moscow (1965).

66BUX/DAI G. V. Buxton, F. S. Dainton, and F. Wilkerson, ''The BrO radical in aqueous solution,'' Chem. Commun. (11), 320–1 (1966); CA 65 8231a; formation and reactions in presence of ultraviolet light.

66CAM C. Campbell, ''Spectroscopic studies of bromine oxides,'' Ph.D. thesis, Cambridge, England (1966); full citation is not available at this time.

66CAR/LEV A. Carrington and D. H. Levy, ''Electron resonance studies of free radicals in the gas phase. Detection of ClO, BrO, and NS,'' J. Chem. Phys. **44**(3), 1298–9 (1966); CA 64 15218a; magnetic resonance absorption, ESR of BrO.

66CHA/BOY J. W. Chase and G. E. Boyd, ''Radiolysis of the crystal alkaline earth bromates by cobalt-60 γ-rays,'' J. Phys. Chem. **70**, 1031–6 (1966); proposed formation of BrO_2.

66SPR/PIM R. D. Spratley and G. C. Pimentel, ''The $[p-\pi^*]\sigma$ and $[s-\pi^*]\sigma$ bonds. FNO and O_2F_2,'' J. Am. Chem. Soc. **88**, 2394–7 (1966); CA 65 3106b; structure.

66VED/GUR V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye. L. Frankevich, *Bond Energies, Ionization Potentials, and Electronic Affinities* (Edward Arnold, London, 1966), p. 33 (English translation of Russian 1962 publication); dissociation energy, review.

67CAR A. Carrington, ''Electron resonance of gaseous free radicals,'' Proc. R. Soc. London, Ser. A **302**(1470), 291–304 (1967); CA 68 109411q; ESR.

67CAR/LEV A. Carrington and D. H. Levy, ''Electron resonance of free radicals in the gas phase,'' J. Phys. Chem. **71**(1), 2–11, discussion 11–12 (1967); CA 67 69326m; EPR.

67CAR/LEV2 A. Carrington, D. H. Levy, and T. A. Miller, "Stark effect in gas-phase electron resonance. The dipole moments of ClO, BrO, SH, and $^1\Delta$ SO," J. Chem. Phys. **47**(10), 3801–9 (1967); CA 68 34133q; EPR, dipole moment.

67CAR/LEV3 A. Carrington, D. H. Levy, and T. A. Miller, "Double quantum transitions in gas-phase electron resonance," J. Chem. Phys. **47**(11), 4859–60 (1967); CA 68 64047q; EPR.

67CAR/LEV4 A. Carrington, D. H. Levy, and T. A. Miller, "Stark-modulated gas phase electron resonance cavity," Rev. Sci. Instrum. **38**(8), 1183–4 (1967); CA 68 64426e; EPR.

68BUX/DAI G. V. Buxton and F. S. Dainton, "The radiolysis of aqueous solutions of oxybromine compounds: the spectra and reactions of BrO and BrO_2," Proc. R. Soc. London, Ser. A **304**(1479), 427–39 (1968); CA 68 110274d; radiolysis, formation, Br_2O_2 as an intermediate.

68CAM/JON C. Campbell, J. P. M. Jones, and J. J. Turner, "Spectroscopic studies of bromine oxides: the infrared spectrum of solid bromine monoxide," Chem. Commun. (15), 888–9 (1968); CA 69 81958t; force constants, IR spectrum, structure, also for $Br_2{}^{18}O$.

68EDW/GRE J. O. Edwards, E. F. Greene and J. Ross, "From stoichiometry and rate law to mechanism," J. Chem. Educ. **45**, 381–5 (1968); CA 69 24473g; proposed structure ($BrBrO_2$), aqueous solutions, review.

68GAY A. G. Gaydon, *Dissociation energies and spectra of diatomic molecules*, 3rd ed. (Chapman and Hall, London, 1968), p. 265; review, dissociation energy.

68WAG/EVA D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, and S. M. Bailey, "Selected values of chemical thermodynamic properties. Part 1. Tables for the first 23 elements in the standard order of arrangement," NBS-TN-270-3, 31 (1968); enthalpy of formation reported.

69AMI/CZA O. Amichai, G. Czapaki, and A. Treinin, "Flash photolysis of the oxybromine anions," Isr. J. Chem. **7**(3), 351–9 (1969); CA 71 118332d; formation in photolysis of bromate and bromite.

69BAR/GIL F. Barat, L. Gilles, B. Hickel, and J. Sutton, "Flash photolysis of aqueous solutions of halate ions," J. Chem. Soc. D (24), 1485 (1969); CA 72 61336x; formation in flash photolysis of aqueous bromate.

69BRE/ROS L. Brewer and G. M. Rosenblatt, "Dissociation energies and free energy functions of gaseous monoxides," Adv. High Temp. Chem. **2**, 1–33 (1969); review.

69CAR A. Carrington, "Electron resonance of gaseous diatomic molecules. Magnetic and electric interactions in $^2\Pi$ states," Proc. Colloq. AMPERE (At. Mol. Etud. Radio Elec. 1968) **15**, 23–41 (pub. 1969); CA 71 130594y; EPR.

69IP/BUR J. K. K. Ip and G. Burns, "Recombination of Br atoms by flash photolysis over a wide temperature range. II. Br_2 in He, Ne, Ar, Kr, N_2, and O_2," J. Chem. Phys. **51**, 3414–24 (1969); CA 71 129273m; rate constants.

69JEN/ZIE P. W. Jennings and T. D. Ziebarth, "Mechanism of the modified Hunsdiecker reaction," J. Org. Chem. **34**(10), 3216–7 (1969); CA 71 123267r; intermediate in Hunsdiecker reaction.

69POW/JOH F. X. Powell and D. R. Johnson, "Microwave spectrum of the BrO free radical," J. Chem. Phys. **50**(10), 4596 (1969); CA 71 34844j; microwave spectrum, ^{79}BrO and ^{81}BrO data.

70AMI/TRE O. Amichai and A. Treinen, "Oxybromine radicals," J. Phys. Chem. **74**(20), 3670–4 (1970); CA 73 104276t; formation in the photolysis and radiolysis of bromate.

70BEG/SUB A. Begum, S. Subramanuan, and M. C. R. Symons, "Oxides and oxyions of the nonmetals. XI. Electron spin resonance study of the bromate radical in γ-irradiated potassium bromate," J. Chem. Soc. (6), 918–21 (1970); CA 72 138214r; EPR in potassium bromate during radiolysis.

70BLA/BRO D. A. Blake, R. J. Browne, and G. Burns, "Interaction potentials involving Br atoms," J. Chem. Phys. **53**, 3320–3 (1970); CA 73 113370w; enthalpy of formation.

70BRO/BUR J. Brown and G. Burns, "Decomposition of bromine monoxide studied by kinetic spectroscopy," Can. J. Chem. **48**(22), 3487–90 (1970); CA 74 25483a; kinetics and mechanism of decomposition.

70CAR/DYE A. Carrington, P. N. Dyer, and D. H. Levy, "Gas-phase electron resonance spectra of bromosyl iodosyl," J. Chem. Phys. **52**(1), 309–14 (1970); CA 72 49474h; ground state configuration, splitting, rotational constant, EPR.

70CLY/CRU M. A. A. Clyne and H. W. Cruse, "Rates of elementary reactions involving the BrO ($X^2\Pi$) and IO ($X^2\Pi$) radicals. 1. Formation and decay of the BrO radical," Trans. Faraday Soc. **66**(9), 2214–26 (1970); CA 73 70238q; kinetics of formation and disproportionation, structure.

70CLY/CRU2 M. A. A. Clyne and H. W. Cruse, "Rates of elementary reactions involving the BrO ($X^2\Pi$) and IO ($X^2\Pi$) radicals. 2. Reactions of the BrO and IO radicals," Trans. Faraday Soc. **66**(9), 2227–36 (1970); CA 73 70239r; reaction with nitrogen dioxide.

70COL/COS M. A. Collins, M. M. Cosgrove, and G. P. Bettertidge, "Bromine dioxide center in irradiated zinc bromate," J. Phys. B **3**(5), L48–L52 (1970); CA 73 50570p; ESR in γ-irradiated zinc bromate, $^{79}BrO_2$ and $^{81}BrO_2$.

70DAR B. de B. Darwent, "Bond dissociation energies in simple molecules," NSRDS-NBS **31**, 1–48 (1970); CA 72 9385e; review, dissociation energy.

70SER/ZAK L. V. Serikov, Yu. A. Zakharov, and A. A. Vasil'ev, "Radiolysis of alkali metal halates," Tr. Mehvuz. Konf. Radiats. Fiz. **1967**, 321–5 (1970); Ref. Zh., Khim. 1971, Abstr. No. 21B1193; CA 77 95304d; EPR study, formation of BrO_3 during radiolysis.

70TOM/STU R. E. Tomalesky and J. E. Sturm, "Bromine monoxide from the flash photolysis of bromine-nitrous oxide and bromine-nitrogen dioxide mixtures," J. Chem. Phys. **52**(1), 472–3 (1970); CA 72 61332t; formation.

71BYB J. R. Byberg, "ESR spectra from paramagnetic centers in irradiated potassium perbromate," J. Chem. Phys. **55**(10), 4867–72 (1971); CA 75 156727b; EPR in potassium perbromate.

71BYF/CAR C. R. Byfleet, A. Carrington, and D. K. Russell, "Electric dipole moments of open-shell diatomic molecules," Mol. Phys. **20**(4), 271–8 (1971); CA 74 147751g; dipole moment, EPR.

71CLY/CRU M. A. A. Clyne and H. W. Cruse, "Studies of ground-state $^2P_{3/2}$ halogen atoms using atomic resonance absorption," Trans. Faraday Soc. **67**, 2869–85 (1971); CA 75 145664e; kinetics, cross-sections.

71KAU/KOL M. Kaufman and C. E. Kolb, "Molecular beam analyzer for identifying transient intermediates in gaseous reactions," Chem. Instrum. **3**(2), 175–89 (1971); CA 76 76557b; detection.

71MIL T. A. Miller, "Alternative explanation for anomalous molecular parameters from electron resonance experiments," J. Chem. Phys. **54**, 3156–61 (1971); CA 74 118155k; questions earlier EPR spectra value of $X^2\Pi_{3/2}$ state.

71OLS K. J. Olsen, "Radiolysis of frozen solutions containing oxybromine anions," Trans. Faraday Soc. **67**(4), 1041–8 (1971); CA 74 132925t; stability in aqueous solution.

71SHE/TUR P. M. A. Sherwood and J. J. Turner, "The reactions of hydrogen atoms with solids at low temperature. Part I. Apparatus, hydrocarbon, and hydrogen cyanide reactions," J. Chem. Soc. A 1971, 2474; no bromine oxides data, only a reference to another study.

72ADL T. Adl, "Electron resonance study of gaseous bromine oxide," Ph.D. thesis, Pennsylvania State University, 92 pp. (1972); Diss. Abstr. Int. B 33(12) [Part 1], 5710; Order No. 73-13945; CA 79 131120t; EPR.

72AMO/YOS T. Amano, A. Yoshinaga, and E. Hirota, "Microwave spectrum of the BrO radical. Equilibrium structure and dipole moment," J. Mol. Spectrosc. **44**(33), 594–8 (1972); CA 78 50058f; molecular constants, ^{79}BrO and ^{81}BrO, microwave spectroscopy.

72BRI B. J. Brisdon, "Oxides and oxyacids of the halogens," Int. Rev. Sci.: Inorg. Chem. Ser One **3**, 21551 (1972); CA 76 R120933x; review.

72BRO/BYF J. M. Brown, C. R. Byfleet, B. J. Howard, and D. K. Russell, "Electron resonance spectra of bromine monoxide, iodine monoxide, and selenium monofluoride in J=5/2 rotational levels," Mol. Phys. **23**(3), 457–68 (1972); CA 77 107377v; EPR.

72BUN N. J. Bunce, "Mercury salt pathway for the degradation of carboxylic acids to alkyl halides using halogen and mercuric salts," J. Org. Chem. **37**(4), 664–9 (1972); CA 76 98849z; reaction with mercuric oxide and pivalic acid.

72BUN2 N. J. Bunce, "Free radical bromination of saturated hydrocarbons using bromine and mercuric oxide," Can. J. Chem. **50**(19), 3109–16 (1972); CA 78 28887d; bromination of alkanes.

72FIE/KOR R. J. Field, E. Koros and R. M. Noyes, "Oscillations in chemical systems. II. Thorough analysis of temporal oscillation in the bromate-cerium-malonic acid system," J. Am. Chem. Soc. **94**(25), 8649–64 (1972); CA 78 48508j; formation of Br_2O_2 in aqueous solution.

72RAO C. G. R. Rao, "Centrifugal distortion constants in bromine trioxide (BrO_3), iodine trioxide (IO_3), and silicon tribromide ($SiBr_3$) molecules," Sci. Cult. **38**(12), 522 (1972); CA 78 166312p; molecular centrifugal distortion constants.

72RAO/SYM K. V. S. Rao and M. C. R. Symons, "Oxides and oxyanions of the nonmetals. XV. Electron spin resonance spectra of selenium and bromine radicals," J. Chem. Soc., Dalton Trans. (2), 147–50 (1972); CA 76 66023k; EPR.

72YAN V. M. Yanishevskii, "On certain regularities in the variation of the fundamental stretching vibration frequencies of diatomic molecules," Opt. Spektrosk. **33**(4), 636–41 (1972); Eng. transl., Opt. Spectrosc. **33**, 349–52 (1972); CA 78 64392x; correlation vibrational frequencies and dissociation energies.

73BYB/SPA J. R. Byberg and J. Spanget-Larsen, "Relation between molecular geometries and nuclear quadrupole coupling constants for some oxy-compounds of bromine and chlorine," Chem. Phys. Lett. **23**, 247–51 (1973); CA 80 125084p; correlation nuclear quadrupole constants and geometry.

73DIX/PAR D. A. Dixon, D. D. Parrish, and D. R. Herschbach, "Molecular beam scattering, general discussion," Faraday Discuss. Chem. Soc. **55**, 385–7 (1973); formation.

73PAN/MIT A. N. Pandey, A. K. Mithal, M. M. Shukla, and G. C. Singh, "Mean amplitudes of vibrational and molecular polarizabilities for some diatomic molecules," Indian J. Pure Appl. Phys. **11**(1), 69–71 (1973); CA 79 47266n; molecular vibrational amplitudes.

73PAR/HER D. D. Parrish and D. R. Herschbach, "Molecular beam chemistry. Persistent collision complex in reaction of oxygen atoms with bromine molecules," J. Chem. Soc. **95**(18), 6133–4 (1973); CA 79 129458r; formation, ground state.

73PAS/POT J. L. Pascal and J. Potier, "Raman spectrum and structure of bromine dioxide," J. Chem. Soc., Chem. Commun. (13), 446–7 (1973); CA 79 98776m; Raman spectra, structure is dimeric, Br_2O_4 with a Br–Br bond.

73SOL/DOR D. V. Sokol'skii, Ya. A. Dorfman, and T. L. Rakitskaya, "Induction period in the reduction of sodium bromate by phosphine," Zh. Fiz. Khim. **47**, 59–61 (1973); Russ. J. Phys. Chem. **47**, 31–2 (1973); CA 79 35500w; intermediate in aqueous solutions.

74BYB/KIR J. R. Byberg and B. S. Kirkegaard, "ESR spectra of BrO_3 and BrO_3^{2-}," J. Chem. Phys. **60**(7), 2594–97 (1974); EPR.

74CAH/RIL R. W. Cahill and J. F. Riley, "Bromine oxide (BrO) disappearance in the pulse radiolysis of molecular oxygen + molecular bromine and nitrogen dioxide + molecular bromine systems," Radiat. Res. **58**(1), 25–37 (1974); CA 80 151056a; formation, disappearance.

74DHA/CLE A. I. Dhar and F. F. Cleveland, "Bond strengths and other constants for diatomic molecules. IV. Calculated values of the energies at zero Kelvin, energies equilibrionic, and constants in the exponential part of the Morse potential energy function, for bonds of the types B-C, B-D, and B-E," Spectrosc. Mol. **23**(268), 42–4 (1974); CA 82 7815w; calculation of force constants, dissociation energies, and vibrational frequencies.

74DHA/CLE2 A. I. Dhar and F. F. Cleveland, "Bond strengths and other constants for diatomic molecules. V. Calculated values of the bond strengths, and of the quantities C_f (force-constant ratio) and C_w (bond-energy ratio), for molecules of several bond types," Spectrosc. Mol. **23**(269), 48–9 (1974); CA 82 7814v; calculation of force constants, dissociation energies, and vibrational frequencies.

74LOV/TIE F. J. Lovas and E. Tiemann, "Microwave spectral tables. I. Diatomic molecules," J. Phys. Chem. Ref. Data **3**(3), 609–769 (1974); CA 82 104977h; review, microwave spectral data.

74PAS/PAV J. L. Pascal, A. C. Pavia, J. Potier, and A. Potier, "New bromine oxide Br_2O_3," C. R. Acad. Sci., Ser. C **279**(1), 43–6 (1974); CA 81 98807p; thermal decomposition.

74SCH J. Schneider, "Internal partition function of two atom molecules in a polynomial representation," Z. Phys. Chem. (Leipzig) **255**(5), 986–96 (1974); CA 82 145259u; coefficients, partition function.

74SOL/KEI I. J. Solomon and J. N. Keith, "Synthesis of halogen compounds in high valence states," AD 775942/6GA, 66 pp. (1974); CA 81 57742v; formation.

74TIS R. Tischer, "5. Constants of Radicals. 5.1 Diatomic Radicals," Landolt-Bornstein New Ser. Group II **6**, 5–90 (1974); review, molecular spectra.

75BYB/LIN J. R. Byberg and J. Linderberg, "ESR Spectra of chloryl and bromyl (BrO_2) exchange coupled to molecular oxygen," Chem. Phys. Lett. **33**(3), 612–5 (1975); CA 83 105899s; EPR of oxygen exchange coupled complex.

75CLY/WAT M. A. A. Clyne and R. T. Watson, "Kinetics studies for diatomic free radicals using mass spectrometry. 3. Elementary reactions involving bromine oxide (BrO [$X^2\Pi$]) radicals," J. Chem. Soc., Faraday Trans. **1** 71(2), 336 50 (1975); CA 82 160763x; kinetics of reactions.

75DAL/LIN E. Dalgard and J. Linderberg, "Energy weighted overlap in magnetic fields. Applications to electron spin resonance problems," Int. J. Quantum Chem., Symp. **9**, 269–77 (1975); CA 84 51901m; structure.

75GIN/SYM I. S. Ginns and M. C. R. Symons, "Radiation mechanisms. I. Inorganic salts in aqueous solutions. Electron spin resonance studies of γ-irradiated aqueous glasses containing oxyanions," J. Chem. Soc., Dalton Trans. (6), 514–21 (1975); CA 83 88617d; formation during radiolysis, EPR.

75RAD/WHI D. St. A. G. Radlein, J. C. Whitehead, and R. Grice, "Reactive scattering of oxygen atoms. Oxygen + diiodine, iodine chloride, dibromine," Mol. Phys. **29**(6), 1813–28 (1975); CA 83 103946f; angular distribution.

75WOF/MCE S. C. Wofsy, M. B. McElroy and Y. L. Yung, "The chemistry of atmospheric bromine," Geophys. Res. Lett. **2**, 215–8 (1975); CA 84 110882f, occurrence of BrO.

76CLY/MON M. A. A. Clyne, P. B. Monkhouse, and L. W. Townsend, "Reactions of oxygen (O ^3P_J) atoms with halogens: The rate constants for the elementary reactions O+BrCl, O+Br_2, and O+Cl_2," Int. J. Chem. Kinet. **8**(3), 425–49 (1976); CA 85 25845x; reaction with O, kinetics.

76MOI/YUR F. B. Moin, Ya. P. Yurkevisc and V. M. Drogovvishkii, "Reaction kinetics of atomic oxygen with chlorine and bromine," Dokl. Akad. Nauk SSSR **226**(4), 866–8 (1976).

76HER/SCH C. Herbo, G. Schmitz and M. Van Glabbeke, "Belousov oscillating reaction. 1. Kinetics of the bromate-cerium (III) reaction," Can. J. Chem. **54**, 2628–38 (1976); CA 85 167261c; Br_2O_2 as an intermediate in aqueous solution.

76ODY/NEC K. Ody, A. Nechvatal, and J. M. Tedder, "Liquid-phase bromination of bromo-butane: variation of the ratio of 1,2- to 1,3-dibromobutanes produced," J. Chem. Soc., Perkins Trans. **2** (5), 521–4 (1976); CA 84 179208h; mechanism of the bromination of halobutanes.

76PAS/PAV J. L. Pascal, A. C. Pavia, J. Potier, and A. Potier, "Synthesis and Raman structural analysis of an isomeric form of dibromine tetroxide (Br_2O_4(B)). Geometric structure of this isomer and of bromine trioxide," C. R. Hebd. Seances Acad. Sci., Ser. C **280**(10), 661–4 (1976); CA 83 18208x; Raman spectra, structure, reactions with ozone.

76PAS/PAV2 J. L. Pascal, A. C. Pavia, J. Potier, and A. Potier, "Synthesis and Raman spectroscopic study of bromine hemipentoxide," C. R. Hebd. Seances Acad. Sci., Ser. C **282**(1), 53–6 (1976); CA 84 98742a; preparation, polymeric structure.

77CLY/CUR M. A. A. Clyne and A. H. Curran, "Reactions of halogen atoms, free radicals, and excited states," Gas Kinet. Energy Transfer **2**, 239–95 (1977); review of kinetics.

77CLY/WAT M. A. A. Clyne and R. T. Watson, "Kinetic studies of diatomic free radicals using mass spectrometry. Part 4. The bromine atom + chlorine dioxide radical and bromine oxide radical + chlorine oxide radical reactions," J. Chem. Soc., Faraday Trans. **1** 73(8), 1169–87 (1977); CA 87 173377c; reactions, thermodynamics.

77GIL/GAR H. M. Gillespie, J. Garraway, and R. J. Donovan, "Reaction of atomic oxygen (2^1D_2) with halomethanes," J. Photochem. **7**(1), 29–40 (1977); CA 87 60675e; formation.

77GLI C. Glidewell, "Bond energy terms in oxides and oxo-anions," Inorg. Chim. Acta **24**(2), 149–57 (1977); CA 87 157428q; bond energy, dissociation energy.

77LEE/BEN P. A. Lee and G. Beni, "New method for the calculation of atomic phase shifts: application to extended x-ray absorption fine structure (EXAFS) in molecules and crystals," Phys. Rev. B **15**(6), 2862–83 (1977); CA 86 163150p; bond length, spectroscopy.

77PAS/PAV J. L. Pascal, A. C. Pavia, J. Potier, and A. Potier, "Structural studies of bromine oxides by Raman laser spectroscopy," Proc. Int. Conf. Raman Spectrosc. 5th (1976), 120–1 (pub. 1977); CA 87 210447y; Raman spectra, structure, thermal decomposition.

77SAS/RAO D. L. Sastry and K. V. S. R. Rao, "ESR study of γ-irradiated cadmium bromate dihydrate," Proc. Nucl. Phys. Solid State Phys. Symp. 20C, 566 (1977); CA 90 112598r; EPR in γ-irradiated cadmium bromate dihydrate.

77TAD/SHI K. Tado, T. Shioda, and K. Tanaka, "Removal of halogen gas from waste gas," J. Kokai Tokkyo Koho JP 7799966 (1977); CA 88 P109907u; reduction.

77VOG/DRE D. Vogt, W. Dreves, and J. Mische, "Energy dependence of differential cross sections in endoergic ion–molecule collision processes of negative ions," Intern. J. Mass Spectrom. Ion Phys. **24**, 285–96 (1977); CA 87 74078z; dissociation energy.

78DUN/DYK S. J. Dunlavey, J. M. Dyke, and A. Morris, "The first ionization potential of the bromine monoxide ($X^2\Pi_i$) radical obtained using photoelectron spectroscopy: Chem. Phys. Lett. **53**(2), 382–4 (1978); CA 88 113036b; IP.

78FOE/SCH H. D. Foersterling, H. Schreiber, and W. Zittlau, "Detection of bromine dioxide (BrO_2) in the Belousov-Zhabotinskii system," Z. Naturforsch. A **33A**(12), 1552–6 (1978); CA 90 94765m; electronic absorption spectra of cerium containing solutions.

78PAS J. L. Pascal, "Contribution to the studies on halogen oxides," Ph.D. Thesis, U.S.T.L. Montpelier, France (1978); oxidation of bromine by ozone, full citation not available at this time.

78ROV/ZHA A. B. Rovinskii and A. M. Zhabotinskii, "Mechanism of the autocatalytic oxidation of cerium (3+) by bromate," Teor. Eksperim. Khim. **14**, 183–92 (1978); Theor. Exptl. Chem. [USSR] 14, 142–50 (1978); CA 89 31486e; Br_2O_2 in aqueous solution yields BrO_2 radicals.

78TEV/SMA D. E. Tevault and R. R. Smardzewski, "Matrix infrared spectrum of the O_2Br radical. Bonding in the O_2X species," J. Am. Chem. Soc. **100**(12), 3955–7 (1978); CA 89 119979d; matrix spectrum, IR.

78TEV/WAL D. E. Tevault, N. Walker, R. R. Smardzewski, and W. B. Fox, "Infrared spectra of the BrO and OBrO free radical and of BrOBr and BrBrO molecules in solid argon at 10 K," J. Phys. Chem. **82**(25), 2728–33 (1978); CA 90 14201m; formation, dimerization, IR spectrum.

78THI/MOH P. Thirugnanasambandam and S. Mohan, "A new look at molecular vibrations: Part II," Indian J. Phys. **52B**(3), 173–8 (1978); CA 90 44141j; molecular vibrations, force constants.

79ADD/DON M. C. Addison, R. J. Donovan, and J. Garraway, "Reactions of $O(2^1D_2)$ and $O(2^3P_J)$ with halomethanes," Faraday Discuss. Chem. Soc. **67**, 286–96 (1979); kinetics.

79CAR/SAH M. Carlier, K. Sahetchian, and L. R. Sochet, "ESR evidence for halogen oxyradical formation in the study of the heterogeneous decomposition of gaseous hydrogen peroxide on halides," Chem. Phys. Lett. **66**(3), 557–60 (1979); CA 92 11795p; formation.

79HUB/HER K. P. Huber and G. Herzberg, *Molecular spectra and molecular structure* (Van Nostrand, New York, 1979), vol. 4, pp. 110–1 (1979); CA 90 B195497f; review, EPR spectra.

79LEU M.-T. Leu, "Rate constant for the reaction bromine oxide (BrO)+nitric oxide−atomic bromine+nitrogen dioxide," Chem. Phys. Lett. **61**(2), 275–9 (1979); CA 90 157672b; reaction with NO(g).

79MIC/PAY J. V. Michael and W. A. Payne, "Absolute rate constants for the reaction of bromine atoms with ozone from 234 to 360 K," Int. J. Chem. Kinet. **11**, 799–809 (1979); rate constant for formation of BrO.

79MIT Mitsubishi Electric Co., "Bromine recovery from wastewater containing bromide ion," Jpn. Kokai Tokkyo Koko **80**, 154, 305 (1979); CA 94 177468a; manufacture from wastewater.

79NOS/BOD Z. Noszticzius and J. Bodiss, "A heterogeneous chemical oscillator. The Belousov-Zhabotinskii-type reaction of oxalic acid," J. Am. Chem. Soc. **101**, 3177–82 (1979); CA 91 90866t; Br_2O_2 as an intermediate in aqueous solution.

79WAT/SAN R. T. Watson, S. P. Sander, and Y. L. Yung, "Pressure and temperature dependence kinetics study of the nitric oxide +bromine oxide − nitrogen dioxide + bromine reaction. Implications for stratospheric bromine photochemistry," J. Phys. Chem. **83**(23), 2936–44 (1979); CA 92 47875d; reaction with NO(g).

80BAU/COX D. L. Baulch, R. A. Cox, R. F. Hapson Jr., J. A. Kerr, J. Troe and R. T. Watson, "Evaluated kinetic and photochemical data for atmospheric chemistry," J. Phys. Chem. Ref. Data **9**(2), 2950471 (1980); kinetics.

80FOE/LAM H. D. Foersterling, H. J. Lanberz, and H. Schreiber, "Formation of bromine dioxide in the Belousov-Zhabotinsky-system investigation of the bromous acid ($HBrO_2$)/bromate reaction," Z. Naturforsch. A **35A**(12), 1354–60 (1980); CA 94 72271c; formation.

80FOE/LAM2 H. D. Foersterling, H. Lamberz, and H. Schreiber, "Formation of bromine oxide (BrO_2) in the Belousov-Zhabotinsky system investigation of the cerium (3^-)/bromate reaction," Z. Naturforsch. A **35A**(3), 329–31 (1980); CA 92 221569u; formation.

80JAF/MAI S. Jaffe and W. K. Mainquist, "Bromine decomposition of ozone," J. Phys. Chem. **84**, 3277–80 (1980); CA 93 228487v; dissociation, transition states.

80KOL L. Kolditz, "Bromine oxygen compounds," Sitzungsber. Akad. Wiss. DDR Math. Naturwiss. Tech. N14, 11–7 (1980); CA 94 166675q; review, formation.

80LOE/MIL A. Loewenschuss, J. C. Miller, and L. Andrews, "Argon matrix absorption spectra of chlorine monoxide, bromine monoxide, iodine monoxide, and emission spectra of iodine monoxide," J. Mol. Spectrosc. **80**(2), 351–62 (1980); CA 93 16053a; vibrational analysis from absorption and emission spectra.

80MOL/MOL L. T. Molina and M. J. Molina, "Impact of brominated compounds on the stratosphere," EPA-600/9-80-003 [Proc. Conf. Methyl Chloroform Other Halocarbon Pollut.] 10/1-10/6 (1980); CA 94 144590f; in stratosphere.

80NIC M. Nicolet, "The chemical equations of stratospheric and mesospheric ozone." FAA-EE-80-20 [Proc. NATO Adv. Study Inst. Atmos. Ozone: Var. Hum. Influences], 823–64 (1980); CA 94 160302u; AD A088889; in atmosphere.

80SAN S. P. Sander, "Kinetic studies of bromine-monoxide and methylperoxy free radicals by flash photolysis," Ph.D. thesis, California Institute of Technology, 259 pp. (1980); CA 93 140860a; Diss Abstr. Int. B 40(12, Pt. 1), 5698; Order No. 8012213; full dissertation not available at this time, reaction kinetics.

80SED/LAZ W. A. Sedlacek, A. L. Lazrus, and B. W. Gandrud, "Measurement of stratospheric bromine," FAA-EE-80-00 [Proc. NATO Adv. Study Inst. Atmos. Ozone: Var. Hum. Influences], 273–80 (1980); CA 94 195482e; AD A08889; determination in stratosphere.

80SUB/LOD M. S. Subhano and S. F. Lodhi, "A mechanism for the photolytic decomposition of hypobromite in aqueous solution at 365 nm, 313 nm, and 253.7 nm," Rev. Roum. Chim. **25**(11-12), 1567–78 ,(1980); CA 95 141909b; formation.

80VEL/DUR I. Veltman, A. Durkin, D. J. Smith, and R. Grice, "Reactive scattering of hydroxyl radicals: OH + Br_2 " Mol. Phys. **40**, 213–24 (1980); CA 93 156174r; structure in Ar matrix.

80YUN/PIN Y. L. Yung, J. P. Pinto, R. T. Watson and S. P. Sander, "Atmospheric bromine and ozone perturbations in the lower stratosphere," J. Atmos. Sci. **37**, 339–53 (1980).

81BAR/COH M. Barnett, E. A. Cohen, and D. A. Ramsay, "The A $^2\Pi_i$–$X^2\Pi_i$ absorption spectrum of bromine oxide (BrO)," Can. J. Phys. **59**(12), 1908–16 (1981); CA 96 94301f; electronic absorption spectrum, ^{81}BrO.

81BOH/SEN M. C. Bohm, K. D. Sen, and P. C. Schmidt, "Molecular orbital electro- negativity," Chem. Phys. Lett. **78**(2), 357–60 (1981); CA 94 163058e; electronegativity.

81BRO/HOB R. J. Browett, J. H. Hobson, F. E. Davidson and R. Grice, "Reactive scattering of a supersonic oxygen atom beam O + Cl_2 at threshold," Mol. Phys. **43**, 113–21 (1981); CA 95 139050w; BrBrO detected in Ar matrix.

81CLY/MAC M. A. A. Clyne and A. J. Macrobert, "Kinetic studies of free radical reactions by mass spectroscopy. II. The reactions of SO + ClO, SO + OClO, and SO + BrO," Int. J. Chem. Kinet. **13**(2), 187–97 (1981); CA 94 91106u; reaction with SO(g).

81COH/PIC E. A. Cohen, H. M. Pickett, and M. Geller, "The rotational spectrum and molecular parameters of bromine monoxide in the $^2\Pi_{3/2}$ state," J. Mol. Spectrosc. **87**(2), 459–70 (1981); CA 95 52007p; microwave spectrum, molecular constants.

81DON/ZEL A. F. Donodov, V. V. Zelenov, and V. L. Tal'roze, "Mechanism of reactions in the oxygen + ozone + bromine system," Kinet. Katal. **22**(1), 245–7 (1981); CA 94 128159s; formation, decay kinetics.

81DOR/MEH S. Doraiswamy and S. C. Mehrotra, "The collision-induced linewidths of chlorine and bromine monoxide perturbed by nitrogen," JSR, J. Geophys. Res., Sect. C **86**(C6), 5381–2 (1981); CA 95 51875h; collision-induced linewidths.

81GRO/LAU M. Grodzicke, S. Lauer, A. X. Trautwein, and A. Vera, "Application of molecular orbital calculations to Moessbauer and NMR spectroscopy of halogen-containing compounds," Adv. Chem. Ser. **194** (Moessbauer Spectrosc. Its Chem. Appl.), 3–37 (1981); CA 96 43242e; dipole moment.

81MCK A. R. W. McKellar, "Laser magnetic resonance spectrum of bromine oxide (BrO) ($^2\Pi_{1/2}$–$^2\Pi_{3/2}$)," J. Mol. Spectrosc. **86**(1), 43–54 (1981); CA 94 112118s; laser magnetic resonance spectrum, ^{79}BrO and ^{81}BrO.

81MEN/SAT A. Menon and N. Sathyamurthy, "Negative activation energy for the Cl(Br)O + NO−Cl(Br) + NO_2 reactions," J. Phys. Chem. **85**(8), 1021–3 (1981); CA 94 198165q; reaction with NO(g).

81RAY/WAT G. W. Ray and R. T. Watson, "Kinetics study of the reactions of nitric oxide with oxygen fluoride, chlorine oxide, bromine oxide, and iodine oxide at 298 K," J. Phys. Chem. **85**(20), 2955–60 (1981); CA 95 139403p; reaction with NO(g).

81SAN/RAY S. P. Sander, G. W. Ray, and R. T. Watson, "Kinetic study of the pressure dependence of the BrO + NO_2 reaction at 298 K," J. Phys. Chem. **85**(2), 199–210 (1981); CA 94 91082h; reaction with NO_2(g).

81SAN/WAT S. P. Sander and R. T. Watson, "Kinetics and mechanism of disproportionation of BrO radicals," J. Phys. Chem. **85**, 4000–7 (1981); CA 95 226406k; formation.

81SEG/SUT C. Sehgal, R. G. Sutherland, and R. E. Verralll, "Sonoluminescence from aqueous solutions of bromine and iodine," J. Phys. Chem. **85**(4), 315–7 (1981): CA 94 111776t; sonoluminescence.

82ANT S. Antonik, "Kinetic and analytical study of the oxidation of trifluoro- bromomethane between 450 and 550°C," Bull. Soc. Chim. Fr. (3-4, Pt 1), 83-9 (1982); CA 97 109370z; lack of abstraction reaction.

82BAU/COX D. L. Baulch, R. A. Cox, P. J. Crutzen, R. E. Hampson, J. A. Kerr, J. Troe and R. T. Watson, "Evaluated kinetic and photochemical data for atmospheric chemistry. Supplement 1. CODATA Task Group on Chemical Kinetics," J. Phys. Chem. Ref. Data **11**, 327–496 (1982); review of the kinetics of reaction involving BrO, references a BrO enthalpy of formation value.

82COX/SHE R. A. Cox and D. W. Sheppard, "Rate coefficient for the reaction of bromine oxide with hydroperoxy at 303 K," J. Chem. Soc., Faraday Trans. 2 **78**(8), 1383–9 (1982); CA 97 169579t; reaction with hydroperoxy, kinetics.

82COX/SHE2 R. A. Cox, D. W. Sheppard, and M. P. Stevens, "Absorption coefficients and kinetics of the bromine oxide (BrO) radical using molecular modulation," J. Photochem. **19**(3), 189–207 (1982); CA 97 118110s; formation, spectra.

82FER/SMI D. P. Fernie, D. J. Smith, A. Durkin, and R. Grice, "Reactive scattering of a supersonic oxygen atom beam: O + Br_2," Mol. Phys. **46**, 41–54 (1982); CA 97 98653r; ground state.

82FIE/RAG R. J. Field, N. V. Raghaven, and J. G. Brummer, "A pulse radiolysis investigation of the reactions of bromine dioxide radical (BrO_2) with hexacyanoferrate(II), manganese(II), phenoxide ion, and phenol," J. Phys. Chem. **86**(13), 2443–9 (1982); CA 97 12499k; reduction.

82FOE/LAM H. D. Foersterling, H. J. Lamberz, H. Schreiber, and W. Zittlau, "Bromine dioxide as an intermediate product of the Belousov-Zhabotinskii reaction," Kem. Kozl. **57**(3-4), 283–93 (1982); CA 97 155341p; formation.

82FOE/LAM H. D Foersterling, H. L. Lamberz, H. Schreiber, and W. Zittlau, "Bromine dioxide (BrO_2) as an intermediate in the Belousov-Zhabotinskii reaction," Acta Chim. Acad. Sci. Hung. **110**(3), 251–60 (1982); CA 97 188870p; formation.

82MUK/KHI V. N. Mukhin, B. A. Khisamov, and A. G. Kotov, "Radiation-induced formation of paramagnetic centers in ionic crystals," Khimn. Fiz. (12), 1637–41 (1982); CA 101 101095u; formation of paramagnetic center.

82WAG/EVA D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall, "The NBS tables of chemical thermodynamic properties. Selected values for inorganic and C_1 and C_2 organic substances in SI units," J. Phys. Chem. Ref. Data 11 Suppl. No. 2, 2–50 (1982); CA 99 B219862k; enthalpy of formation reported, supersedes 65WAG/EVA.

83ALL S. D. Allen, "Spectroscopy and photochemical studies of the bromine oxides," Ph.D. thesis, Nottingham, England (1983); full citation not available at this time.

83BUS/SIB R. J. Buss, S. J. Sibener and Y. T. Lee, "Reactive scattering of $O(^3P) + CF_3I$," J. Phys. Chem. **87**(24), 4840 (1983); ground state assumed by analogy with other halogen oxides.

83BUT/MOR N. I. Butkovskaya, I. I. Morozov, V. L. Tal'rose, E. S. Vasiliev, "Kinetic studies of the bromine-oxygen system: a new paramagnetic particle, bromine dioxide," Chem. Phys. **79**(1), 21–30 (1983); CA 99 146907s; formation, structure.

83FIE/RAG R. J. Field, N. N. Raghavan, and J. G. Brunimer, "Pulse radiolysis study of the reaction between the bromine dioxide radical and hexacyanoferrate(4−) ion, manganese(II), phenoxide ion, or phenol," Kem. Kozl. **59**(1-2), 235–50 (1983); CA 101 237999z; formation and reaction in pulse radiolysis of bromite solutions.

83FOE/LAM H. D. Foersterling, H. J. Lamberz, and H. Schreiber, "Formation of bromine dioxide (BrO_2) in the Belousov-Zhabotinskii reaction of aliphatic alcohols with bromate," Z. Naturforsch. A **38A**(4), 483–6 (1983); CA 99 52982k; formation.

84BAU/COX D. L. Baulch, R. A. Cox, R. F. Hampson Jr., J. A. Kerr, J. Troe, and R. T. Watson, "Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement II. CODATA task group on gas phase chemical kinetics," J. Phys. Chem. Ref. Data 13, 1259–380 (1984); CA 102 152285j; review, kinetics.

84BOL/BAL J. J. Boland and J. D. Baldeschwieler, "The effect of thermal vibrations on extended x-ray absorption fine structure. II," J. Chem. Phys. **81**(3), 1145–59 (1984); CA 101 100730k; thermal vibrations effect on EXAFS.

84BUR/LAW J. K. Burdett, N. J. Lawrence, and J. J. Turner, "Oxygen fluorides, non-metal halides, van der Waals molecules, and related species: a linking theoretical thread," Inorg. Chem. **23**, 2419–28 (1984); CA 101 60416; review.

84BUT/KAW J. E. Butler, K. Kawaguchi, and E. Hirota, "Infrared diode laser spectroscopy of the bromine oxide (BrO) radical," J. Mol. Spectrosc. **104**(2), 372–9 (1984); CA 100 147790z; IR spectrum, ^{79}BrO, ^{81}BrO.

84CLA D. C. Clary, "Rates of chemical reactions dominated by long-range inter-molecular forces," Mol. Phys. **53**(1), 3–21 (1984); CA 101 198902r; reaction with NO(g).

84EPI/LAR N. D. Epiolis, J. R. Larson, and H. H. Eaton, "Common denominator by the MOVB method: the structures of water, hydrogen peroxide, and their derivatives," Croat. Chem. Acta, **57**(5), 1031–53 (1984); CA 102 172905q; MO-VB theory in study of molecular structure.

84JAC M. E. Jacox, "Ground-state vibrational energy levels of polyatomic transient molecules," J. Phys. Chem. Ref. Data 13(4), 945–1068 (1984); CA 103 45024x; review of ground state vibrational levels.

84STE Kobe Steel, "Lubricant coatings for petroleum-drilling pipe threads," Japan 841744699 (1984); CA 102 116422t; lubricant.

84SAS/RAO D. L. Sastry and K. V. S. Rama Rao, "Comparative study of quadrupole coupling constants of BrO_3 and BrO^{-31} paramagnetic radical derived from bromate (BrO_3) ion," Proc. Nucl. Phys. Solid State Phys. Symp. **25C**, 201-2 (1984); CA 102 141172u; quadrupole coupling constants of paramagnetic radicals.

84SAU/TAT J. Sauval and J. B. Tatum, "A set of partition functions and equilibrium constants for 300 diatomic molecules of astrophysical interest," Astrophys. J., Suppl. Ser. **56**(2), 193-209 (1984); CA 101 200866c; equilibrium constant, partition function.

85BEN/KRI V. A. Benderskii and A. G. Krivenko, "Time resolutions of polarograms of intermediate species," Elektrokhimiya **21**(11), 1507–13 (1985); CA 104 58296h; polarograms.

85BJE/BYB N. Bjerre and J. R. Byberg, "Formation of complex defects involving molecular oxygen by electronhole reactions in X-irradiated $KClO_4$ and $KBrO_4$, studied by ESR and IR spectroscopy," J. Chem. Phys. **82**(5), 2206–11 (1985); CA 102 194277p; EPR/IR formation of [XO_2, O_2].

85BYB J. R. Byberg, "Oxidation of bromate ion in solid matrices studied by ESR," J. Chem. Phys. **83**(3), 919–24 (1985); CA 103 147964w; electronic levels within potassium perchlorate.

85BYK/GOR I. B. Bykhalo, E. B. Gordon, A. P. Perminov, and V. V. Filatov, "EPR study of reactions of excited atoms. The atomic oxygen + molecular bromine → bromine monoxide + atomic bromine ($^2P_{1/2}$, $^2P_{3/2}$). Formation of atomic bromine ($^2P_{1/2}$) in the reaction of hydrogen deuterium and fluorine with molecular bromine," Khim. Fiz. **4**, 770–8 (1985); CA 103 60060z; ground and excited states of BrO.

85DUI/HUD M. T. Duignan and J. W. Hudgens, "Multiphoton ionization spectroscopy of chlorine monoxide (ClO) and bromine monoxide (BrO)," J. Chem. Phys. **82**(10), 4426–33 (1985); CA 103 14011m; ionization spectra.

85FOE/LAM H. D. Foersterling, H. J. Lamberz, and H. Schreiber, "Kinetics of the cerium (3+)/bromine oxide (BrO_2) reaction in sulfuric acid medium," Z. Naturforsch. A: Phys., Phys. Chem., Kosmophys. **40A**(4), 368–72 (1985); CA 102 210074c; redox reaction with cerium(III) in sulfuric acid.

85POY/PIC R. L. Poynter and H. M. Pickett, "Submillimeter, millimeter, and microwave spectral line catalog," Appl. Opt. **24**(14), 2235–40 (1985); CA 103 78568f; submillimeter, millimeter, microwave spectral line catalog.

85STE H. J. Sternal, "Device for testing blood alcohol content," Ger. 3418373 (1985); CA 104 47016r; pill containing BrO_2 for alcohol determination.

86BEN/KRI V. A. Benderskii, A. G. Krivenko, and N. V. Fedorich, "Electrode reactions of intermediate species formed during the reduction of the bromate anion on mercury," Elektrokhimiya **22**(6), 728–34 (1986); CA 105 68947f; reduction on mercury.

86BRU/AND W. H. Brune and J. G. Anderson, "In situ observations of midlatitude stratospheric chlorine oxide (ClO) and bromine oxide (BrO)," Geophys. Res. Lett. **13**(13), 1391–4 (1986); CA 106 87998k; in stratosphere.

86BRU/STI J. Brunning and L. Stief, "Rate constant for the reaction sulfur monoxide + bromine monoxide → sulfur dioxide + atomic bromine," J. Chem. Phys. **85**(5), 2591–4 (1986); CA 105 159527k; kinetics of reaction with SO(g).

86BYB J. R. Byberg, "ESR study of the complexes chlorine oxide −molecular oxygen (ClO,O_2) and bromine oxide −molecular oxygen (BrO,O_2) formed by decomposition of chlorate and bromate anions in solid potassium perchlorate," J. Chem. Phys. **84**(8), 4235–42 (1986); CA 104 234114h; complex with molecular oxygen.

86BYB2 J. R. Byberg, "ESR study of the formation of complex defects involving molecular oxygen by electron-hole reactions in x-irradiated potassium chlorate and potassium bromate," J. Chem. Phys. **84**(11), 6204–9 (1986); CA 105 32826b; EPR of complex defects.

86GIN M. L. Ginter, "Spectral studies related to dissociation of hydrogen bromide, hydrogen chloride, and bromine monoxide," NASA-CR-176698, 92 pp. (1986); CA 105 177657g; dissociation.

86HIL/MCC G. W. Hills, W. J. McCoy, and R. E. Muenchausen, "Infrared spectroscopy using optogalvanic detection of a radio-frequency discharge," AIP Conf. Proc. **146** [Adv. Laser Sci.-1], 456–7 (1986); CA 105 143232z; detection technique.

86HUI/NET R. E. Huie and P. Neta, "Kinetics of one-electron transfer reactions involving chlorine dioxides and nitrogen dioxide," J. Phys. Chem. **90**(6), 1193–8 (1986); CA 104 116829x; 1-electron transfer reactions.

86KRE/FAB B. C. Kreuger and P. Fabian, "Model calculations about the reduction of atomospheric ozone by different halogenated hydrocarbons," Ber. Bunsen-Ges. Phys. Chem. **90**(11), 1062–6 (1986); CA 106 37743c; formation.

86MCE/SAL M. B. McElroy, R. J. Salawitch, and S. V. Wofsy, "Antarctic ozone: mechanism for the spring decrease," Geophys. Res. Lett. **13**(12), 1296–9 (1986); CA 106 36327h; Antarctic stratosphere.

86MOZ M. Mozurkewich, "Reactions of hydroperoxo with free radicals," J. Phys. Chem. **90**(10), 2216–21 (1986); CA 104 194019x; reaction with hydroperoxo.

86RAZ/DOD V. V. Raznikov, A. F. Dodonov, and V. V. Zelenov, "Disentangling the fine structure of ionization efficiency curves," Int. J. Mass Spectrom. Ion Processes **71**(1), 1–27 (1986); CA 104 142768s; ionization efficiency curves.

86SAN S. P. Sander, "Kinetics and mechanism of the IO-IO reaction," J. Phys. Chem. **90**, 2194–9 (1986); CA 104 194017v; formation.

86THO R. C. Thompson, "Reaction mechanisms of the halogens and oxo-halogen species in acidic, aqueous solution," Adv. Inorg. Bioinorg. Mech. **4**, 65–106 (1986); CA 105 214454m; review, intermediate in aqueous solutions.

86TUN/KO K. K. Tung, M. K. W. Ko, J. M. Rodriguez, amd N. D. Sze, "Are Antartic ozone variations a manifestation of dynamics or chemistry?" Nature (London) **322**(6082), 811–4 (1986); CA 105 137411r; reaction with ClO(g).

86UMA/RAM Y. Umasasidhar, S. Ramaprabhu, and K. V. S. Rama Rao, "Investigation of EFG parameters at the halogen site in XO_3 and XO_3^{2-} radicals (X=chlorine, bromine) in certain inorganic solids," Z. Naturforsch. A: Phys., Phys. Chem., Kosmophys. **41A**(1-2), 169–70 (1986); CA 105 12341m; thermal vibrations effects on EXAFS.

87ALL/POL S. D. Allen, M. Poliakoff, and J. J. Turner, "Photochemistry of an ozone-bromine complex; the IR spectrum of matrix isolated Br_2O," J. Mol. Struct. **157**, 1–15 (1987); CA 106 186247w; critique of earlier vibrational data.

87BAS/GAV N. G. Basov, V. F. Gavrikov, S. A. Pozdneev and V. A. Shcheglov, "Possible expansion of the spectral emission range of electronic-transition chemical lasers," Sov. J. Quantum Electron. **17**(9), 1139–52 (1987).

87ELO/RYN A. Elofson, K. Rynefors, and L. Holmlid, "Monte Carlo simulation of RRKM unimolecular decomposition in molecular beam experiments. V. Product oxygen halide (OX) angular and energy distributions from atomic oxygen (^3P) + X_2 (X=bromine, iodine)," Chem. Phys. **118**(1), 1–16 (1987); CA 108 44232e; unimolecular decomposition.

87FLE/SWA S. J. Fleming and C. P. Swann, "Color additives and trace elements in ancient glasses: specialized studies using PIXE spectrometry," Nucl. Instrum. Methods Phys. Res., Sect. B **B22**(1-3), 411-8 (1987); CA 106 195455q; determination.

87HIL/CIC A. J. Hills, R. J. Cicerone, J. G. Calvert, and J. W. Birks, "Kinetics of the bromine monoxide + chlorine monoxide reactions and implications for stratospheric ozone," Nature (London) **328**(6129), 405-8 (1987); CA 107 100125r; full citation not available at this time, reaction with ClO(g), kinetics.

87LOE/AND L. M. Loewenstein and J. G. Anderson, "Reactions of radicals with halogen molecules: a frontier orbital interpretation," J. Phys. Chem. **91**, 2993–7 (1987); CA 106 202539a; proposed cyclic BrBrO structure.

87SWA/FLE C. P. Swann and S. J. Fleming, "PIXE spectrometry in archaeometry: the development of a system with high spatial resolution," Nucl. Instrum. Methods Phys. Res., Sect. B **B22**(1-3), 407–10 (1987); CA 106 195454p; determination.

88BAR/BOT L. A. Barrie, J. W. Bottenheim, R. C. Schnell, P. J. Crutzen, and R. A. Rasmussen, "Ozone destruction and photochemical reactions at polar sunrise in the lower Arctic atmosphere," Nature **334**(6178), 138–41 (1988); CA 109 115299r; in air, ozone destruction in relation to; deals with BrO (not Br_2O_5).

88BAR/SOL J. W. Barrett, P. M. Solomon, R. L. DeZafra, M. Jaramillo, L. Emmons, and A. Parrish, "Formation of the Antractic ozone hole by the chlorine monoxide dimer mechanism," Nature (London) **336**(6198), 455–8 (1988); CA 110 99189t; in lower stratosphere.

88BRU/TOO W. H. Brune, D. W. Toohey, J. G. Anderson, W. L. Starr, J. F. Vedder, and E. F. Danielson, "In situ northern mid-latitude observations of chlorine monoxide, ozone, and bromine monoxide in the wintertime lower stratosphere," Sci. **242**(4878), 558–62 (1988); CA 110 26966j; in lower stratosphere.

88COS/TEN R. C. Costen, G. M. Tennille, and J. S. Levine, "Cloud pumping in a one- dimensional photochemical model," J. Geophys. Res. D: Atmos. **93**(D12), 15941–54 (1988); CA 110 158021g; in troposphere; deals with BrO (not Br_2O_5).

88FLE/SWA S. J. Fleming and C. P. Swann, "The Bartol PIXE microprobe facility: recent applications in archaeology," Nucl. Instrum. Methods Phys. Res., Sect. B **B30**(3), 444–53 (1988); CA 108 166628j; determination in archaeological artifacts.

88HIL A. J. Hills, "Kinetics investigations of atmospheric chemical reactions," Ph. D. thesis, University of Colorado, 108 pp. (1987); Univ. Microfilms Int., Order No. DA8723465; Diss. Abstr. Int. B **48**(10), 2951 (1988); CA 107 100125s; reaction with ClO(g).

88HIL/CIC A. J. Hills, R. J. Cicerone, J. G. Calvert, and J. W. Birks, "Temperature dependence of the rate constant and product channels for the bromine oxide + chlorine oxide reaction," J. Phys. Chem. **92**(7), 1853–8 (1988); CA 108 157109p; kinetics of reaction with ClO(g).

88IGE/STO G. Igel-Mann, H. Stoll, and H. Preuss, "Pseudopotential study of monohydrides and monoxides of main group elements potassium through bromine," Mol. Phys. **65**(6), 1329–36 (1988); CA 111 202162a; calculation of r_e, ω_e, and D_e.

88NET/HUI P. Neta, R. E. Huie, and A. B. Ross, "Rate constants for reactions of inorganic radicals in aqueous solution," J. Phys. Chem. Ref. Data **17**(3), 1027–284 (1988); CA 109 R198144k; reactions, review.

88SAL/WOF R. J. Salawitch, S. C. Wofsy, and M. B. McElroy, "Chemistry of OClO in the Antarctic stratosphere: implications for bromine," Planet Space Sci. **36**(2), 213–24 (1988); CA 108 226063h; reaction with ClO_2.

88SAN/FRI S. P. Sander and R. R. Friedl, "Kinetics and product studies of the bromine oxide (BrO) + chlrorine oxide (ClO) reaction: implications for Antarctic chemistry," Geophys. Res. Lett. **15**(8), 887–90 (1988); CA 109 173873j; reaction with ClO(g).

88SIN M. Singh, "Thirty-one new diatomic molecules in cosmic objects spectra," Astrophys. Space Sci. **140**(2), 421–7 (1988); CA 109 82624n; dissociation energy, IP.

88TOO/AND D. W. Toohey and J. G. Anderson, "Formation of bromine chloride ($^3\Pi_u 0^+$) in the reaction of bromine monoxide with chlorine monoxide," J. Phys. Chem. **92**(7), 1705–8 (1988); CA 108 157132r; kinetics of reaction with ClO(g).

88TOO/BRU D. W. Toohey, W. H. Brune, and J. C. Anderson, "Rate constant for the reaction $Br + O_3 \rightarrow BrO + O_2$ from 248 to 418 K: kinetics and mechanism," Intern. J. Chem. Kinet. **20**, 131–44 (1988); CA 108 157114m; reaction, titration with NO, enthalpy of formation.

88TYK R. J. Tykodi, "Estimated thermochemical properties of some noble-gas monoxides and difluorides," J. Chem. Educ. **65**(11), 981–5 (1988); CA 110 220036w; enthalpy of atomization.

88WAH/RAV A. Wahner, A. R. Ravishankara, S. P. Sander, and R. R. Friedl, "Absorption cross section of BrO between 312 and 385 nm at 298 and 223 K," Chem. Phys. Lett. **152**(6), 507–12 (1988); CA 110 66041k; UV absorption cross sections.

89AND/BRU J. G. Anderson, W. H. Brune, S. A. Lloyd, D. W. Toohey, S. P. Sander, W. L. Starr, M. Loewenstein, and J. R. Podolske, "Kinetics of ozone destruction by chlorine oxide and bromine oxide within the Antarctic vortex: an analysis based on in situ ER-2 data," J. Geophys. Res., D: Atmos. **94**(D9), 11480–520 (1989); CA 113 62842m; reactions.

89ATK/BAU R. Atkinson, D. C. Baulch, R. A. Cox, R. F. Hampson Jr., J. A. Kerr, and J. Troe, "Evaluated kinetics and photochemical data for atmospheric chemistry. Supplement III," J. Phys. Chem. Ref. Data **18**, 881–1097 (1989); CA 111 121638h; review, reaction enthalpy.

89ATK/BAU2 R. Atkinson, D. C. Baulch, R. A. Cox, R. F. Hampson Jr., J. A. Kerr, and J. Troe, "Towards a quantitative understanding of atmospheric ozone," Planet. Space Sci. **37**(12), 1605–20 (1989); reactions with ClO.

89AUS/JON J. Austin, R. L. Jones, D. S. McKenna, A. T. Buckland, J. G. Anderson, D. W. Fahey, C. B. Farmer, L. E. Heidt, M. H. Proffitt, and others, "Lagrangian photochemical modeling studies of the 1987 Antarctic spring vortex. 2. Seasonal trends in ozone," J. Geophys. Res. (Atmos) **94**(D14), 16717–35 (1989); CA 114 68161f; in stratosphere.

89BAR/BEC I. Barnes, K. H. Becker, D. Martin, P. Carlier, G. Mouvier, J. L. Jourdain, G. Laverdet, and G. Le Bras, "Impact of halogen oxides on dimethyl sulfide oxidation in the marine atmosphere," ACS Symp. Ser. **393** [Biog. Sulfur Environ.], 464–75 (1989); CA 112 238441a; reaction.

89BOW/BOY G. A. Bowmaker and P. D. W. Boyd, "An SCF-MS-X_α study of the bonding and nuclear quadrupole coupling in oxygen compounds of the halogens," THEOCHEM **60**, 161–75 (1989); CA 112 84498k; bonding, nuclear quadrupole coupling.

89BRU/AND W. H. Brune, J. G. Anderson, and K. R. Chan, "In situ observations of bromine oxide (BrO) over Antarctica: ER-2 aircraft results from 54° S to 72° S latitude," J. Geophys. Res. (Atmos.) **94**(D14), 16639–47 (1989); CA 113 236826b; in stratosphere, deals with BrO (not Br_3O_8).

89CAR/SAN M. A. Carroll, R. W. Sanders, S. Solomon, and A. Schmeltekopf, "Visible and near-ultraviolet spectroscopy at McMurdo Sation, Antarctica. 6. Observations of bromine oxide (BrO)," J. Geophys. Res. (Atmos.) **94**(D14), 16633–8 (1989); CA 113 236825a; in stratosphere, deals with BrO (not Br_3O_8).

89FOE/NOS H. D. Foersterling and Z. Noszticzius, "An additional negative feedback loop in the classical Belousov-Zhabotinsklii reaction: malonyl radical as a second control intermediate," J. Phys. Chem. **93**(7), 2740–8 (1989); CA 110 142188f; reaction.

89FRI/SAN R. R. Friedl and S. P. Sander, "Kinetics and product studies of the reaction chlorine monoxide + bromine monoxide using discharge-flow mass spectrometry," J. Phys. Chem. **93**(12), 4756–64 (1989); CA 111 13080m; reaction with ClO(g).

89KO/ROD M. K. W. Ko, J. M. Rodriquez, N. D. Sze, M. H. Proffitt, W. L. Starr, A. Krueger, E. V. Browell, and M. P. McCormick, "Implications of AAOE observations of the seasonal and interannual behavior of Antarctic ozone," J. Geophys. Res. (Atmos) **94**(D14), 16705–15 (1989); CA 114 68160e; in stratosphere.

89MEL/POU A. Mellouki, G. Poulet, G. Le Bras, R. Singer, J. P. Burrows, and G. K. Moortgat, "Discharge flow kinetic study of the reactions of nitrate radical with bromine, bromine monoxide, hydrogen bromide, and hydrogen chloride," J. Phys. Chem. **93**(24), 8017–21 (1989); CA 111 241084w; kinetics of reaction with NO_3^-, EPR.

89SAN/FRI S. P. Sander and R. R. Friedl, "Kinetics and product studies of the reaction chlorine monoxide + bromine monoxide using flash photolysis-ultraviolet absorption," J. Phys. Chem. **93**(12), 4764–71 (1989); CA 111 15161n; reaction with NO_2.

89SOL/SAN S. Solomon, R. W. Sanders, M. A. Carroll, and A. L. Schmeltekopf, "Visible and near-ultraviolet spectroscopy at McMurdo Station, Antarctica 5. Observations of the diuranal variations of bromine oxide and chlorine dioxide," J. Geophys. Res., D: Atmos. **94**(D9), 11393–403 (1989); CA 113 27063n; in lower stratosphere.

89STA D. M. Stanbury, "Reduction potentials involving inorganic free radicals in aqueous solutions," Adv. Inorg. Chem. **33**, 69–138 (1989); CA 111 162816h.

90BIG/BRO P. Biggs, A. C. Brown, C. Canosa-Mas, P. Carpenter, P. S. Monks, and R. P. Wayne, "The reactions of nitrate radical with atoms and radicals," Phys.-Chem. Behav. Atmos. Pollut., (Proc. Eur. Symp. 1989) 5th, 204-9 (pub. 1990); CA 115 77627k; reactions with nitrate radical.

90BOT/BAR J. W. Bottenheim, L. A. Barrie, E. Atlas, L. E. Heidt, H. Niki, R. A. Reinholt, and P. B. Shepson, "Depletion of lower tropospheric ozone during Arctic spring: the Polar Sunrise Experiment 1988," J. Geophys. Res. (Atmos.) **95**(D11), 18555–68 (1990): CA 115 12675e; in troposphere, deals with BrO (not Br_3O_8).

90DAN/CAR F. Danis, F. Caralp, J. Masanet, and R. Lesclaux, "Kinetics of the reaction bromine monoxide + nitrogen dioxide + M → bromine nitrate + M in the temperature range 263-343 K," Chem. Phys. Lett. **167**(5), 450–6 (1990); CA 113 47316z; reaction with NO_2.

90HAR/WHI G. L. Harlow, C. A. Whitehurst, H. Robards, D. Deville, and B. V. Rao, Ash vitrification—a technology ready for transfer, Proc. Shale Waste Process. Conf. 14th, 143-50 (1990), CA 115 98613t; in vitrified slag.

90JAC M. E. Jacox, "Vibrational and electronic energy levels of polyatomic transient molecules. Supplement," J. Phys. Chem. Ref. Data **19**(6), 1387–1546 (1990); CA 115 263718r; electronic and vibrational energy levels, review.

90JOO F. Jooste, "Stabilized sterilizing or disinfecting halogen-containing composition, method, and apparatus," PCT Int. Appl. WO 90 08,558 (1990); CA 114 P88678h; stable disinfectant containing.

90LEV/OGD W. Levason, J. S. Ogden, M. D. Spicer, and N. A. Young, "Characterization of dibromine oxide (Br_2O) by bromine K-edge EXAFS and IR spectroscopy," J. Am. Chem. Soc. **112**(3), 1019–22 (1990); CA 112 68662d; preparation of Br_2O, decomposition of BrO_2.

90PHI L. F. Phillips, "Collision-theory calculations of rate constants for some atmospheric radical reactions over the temperature range 10-600 K," J. Phys. Chem. **94**(19), 7482–7 (1990); CA 113 135958r; rate constants of reactions.

90POU/LAN G. Poulet, I. T. Lancar, G. Laverdet, and G. Le Bras, "The BrO and ClO reaction and the polar stratospheric ozone," in Phys.-Chem. Behav. Atmos. Pollut. [Proc. Eur. Symp., 5th, eds. G Restelli and G. Angeletti], 190-5 (1990); CA 115 77625h; reaction with ClO(g).

90POU/LAN2 G. Poulet, I. T. Lancar, G. Laverdet, and G. Le Bras, "Kinetics and products of the bromine monoxide + chlorine monoxide reaction," J. Phys. Chem. **94**(19), 278–84 (1990); CA 112 43481f; reaction with ClO(g).

90SAS/HUI L. V. Sastry, R. E. Huie, and P. Neta, "Formation and reactivity of hypophosphite and phosphite radicals and their peroxyl derivatives," J. Phys. Chem. **94**(5), 1895–9 (1990); CA 112 126245h: electron exchange reaction.

90SOL S. Solomon, "Progress towards a quantitative understanding of Antartic ozone depletion," Nature **347**, 347–54 (1990).

90TUR A. A. Turnipseed, "Kinetics of the reactions of bromine monoxide radicals with chlorine monoxide and bromine monoxide, and the chemiluminescent reactions of fluorine with dimethyl sulfide," PB90-256322, 155 pp. (1990); CA 114 172367p; self reaction with ClO(g), kinetics, self disproportionation.

90TUR/BIR A. A. Turnipseed, J. W. Birks, and J. G. Calvert, "Kinetics of the bromine monoxide radical+bromine monoxide radical reaction," J. Phys. Chem. **94**(19), 7477–82 (1990); CA 113 139614y; self disproportionation, Br_2O_2 as an intermediate.

91AND/TOO J. G. Anderson, D. W. Toohey, and W. H. Brune, "Free radicals within the Antarctic vortex: the role of CFC's in Antarctic ozone loss," Sci. **251**(4989), 39–46 (1991); CA 114 128100x; in Antarctic vortex.

91ARS/ZIV M. Arsenovic, M. Zivanovic, and R. Sovljanski, "Weed control on railways in Yugoslavia," Brighton Crop Prot. Conf. - Weeds **3**, 1159–64 (1991); CA 116 250367w.

91BAR/BAS I. Barnes, V. Bastian, K. H. Becker, and R. D. Overath, "Kinetic studies of the reactions of iodine oxide, bromine oxide, and chlorine oxide with dimethyl sulfide," Int. J. Chem. Kinet. **23**(7), 579–91 (1991); CA 115 113768a; reaction.

91BEN/GER C. R. Bennett and J. Gerlach, "Removal of selenium from wastewaters," U.S. Patent No. 5,071,568 (1991); CA 116 P180462x; oxidizing agents.

91JAD/LON D. B. Jadhav and A. L. Londhe, "A portable spectrometer with source intensity variation compensation for visible twilight spectroscopy," Ind. J. Technol. **29**(9), 455–8 (1991); CA 115 286115f; determination in troposphere.

91LAN/LAV I. T. Lancar, G. Laveret, G. Le Bras, and G. Poulet, "Rate constant and products of the bromine oxide + bromine monoxide reaction at 298 K," Int. J. Chem. Kinet. **23**(1), 37–45 (1991); CA 114 172324x; kinetics of recombination.

91MOU/JAK G. H. Mount, R. O. Jakoubek, R. W. Sanders, J. W. Harder, R. Winkler, T. Thompson, and W. Harrop, "New spectroscopic instrumentation for measurement of stratospheric trace species by remote sensing of scattered skylight," Proc. SPIE-Int. Soc. Opt. Eng. **1491** (Remote Sens. Atmos. Chem.), 188–93 (1991); CA 115 286129p; determination in stratosphere, most likely deals BrO (not Br_3O_8).

91MUR D. M. Murphy, "Ozone loss rates calculated along ER-2 flight tracks," J. Geophys. Res. (Atmos.) **96**(D3), 5045–53 (1991); CA 114 210995b; reactions.

91NEU/DOR R. Neuroth, H. P. Dorn, and U. Platt, "High resolution spectral features of a series of aromatic hydrocarbons and bromine oxide (BrO): potential interferences in atmospheric hydroxyl-measurements," J. Atmos. Chem. **12**(3), 287–98 (1991); CA 114 252978d; interference.

91ORL/BUR J. J. Orlando, J. B. Burkholder, A. M. R. Bopegedera, and C. J. Carleton, "Infrared measurements of bromine monoxide ($X^2\Pi_{3/2}$)," J. Mol. Spectrosc. **45**(2), 278–89 (1991); CA 114 110997k; IR spectra, spectral constants.

91SZA/WOJ E. Szabo-Bardos, L. Wojnarovits, and A. Horvath, "Pulse radiolysis studies on hexacyanoferrate(II)-bromate-cyanide system in ethylene glycol-water solutions," J. Radioanal. Nucl. Chem. **147**(2), 215–24 (1991); CA 114 174775u; formation, reactions.

91TUR A. A. Turnipseed, "Kinetics of the reactions of bromine monoxide radicals with chlorine monoxide and bromone monoxide, and the chemiluminescent reactions of fluorine with dimethyl sulfide," Ph.D. thesis, University of Colorado, 151 pp. (1991); Univ. Microfilms Int. Order No. DA9117088; Diss Abstr. Int. B **52**(1), 206–7 (1991); CA 115 240971j; full citation not available at this time, self reaction, reaction with ClO(g).

91TUR/BIR A. A. Turnipseed, J. W. Birks, and J. G. Calvert, "Kinetics and temperature dependence of the bromine monoxide + chlorine monoxide reaction," J. Phys. Chem. **95**(11), 4356–64 (1991); CA 114 235796a; temperature dependence, kinetics.

92FAN/JAC S.-M. Fan and D. J. Jacob, "Surface ozone depletion in Arctic spring sustained by bromine reactions on aerosols," Nature **359**, 522–24 (1992).

92GIL/LEV T. R. Gilson and W. Levason, "Bromine perbromate: synthesis and bromine K-edge EXAFS studies," J. Am. Chem. Soc. **114**(13), 5469–70 (1992); CA 117 19295f; hydrolysis, molecular structure.

92GIL/POL M. K. Gilles, M. L. Polak, and W. C. Lineberger, "Photoelectron spectroscopy of the halogen oxide anions oxygen fluoride ion (1−), oxygen chloride ion (1−), oxygen bromide ion (1−), oxygen iodide ion (1−), chlorine dioxide ion (1−), and iodine dioxide ion(1−)," J. Chem. Phys. **96**(11), 8012–20 (1992); CA 117 79197k; electron affinity.

92MCC/HEN J. C. McConnell, G. S. Henderson, L. Barrie, J. Bottenheim, H. Nikis, C. H. Langford and E. M. J. Templeton, "Photochemical bromine production implicated in Arctic boundary-layer ozone depletion," Nature **355**, 150–52 (1992).

92NOV I. Novak, "Molecular and electronic structure of bromine oxide (Br_2O)," Struct. Chem. **3**(6), 377–9 (1992); CA 118 46210b; ab initio calculation of structure.

92POU/PIR G. Poulet, M. Pirre, F. Maguin, R. Ramaroson, and G. Le Bras, "Role of the bromine oxide + hydroperoxo reaction in the stratospheric chemistry of bromine," Geophys. Res. Lett. **19**(23), 2305–8 (1992); CA 118 216913c; kinetics.

92ROS/TIM V. V. Rosanov, Yu. M. Timofeev, J. Burrows, and W. Scheider, "Sensitivity of transmission functions in tangential directions to variations in atmospheric gas composition," Izv. Akad. Nauk, Fiz. Atmos. Okeana **28**(7), 714–20 (1992); CA 119 143361e; detection of BrO, ClO and OClO.

92WAH/SCH A. Wahner and C. Schiller, "Twilight variation of vertical column abundances of chlorine dioxide and bromine monoxide in the North Polar region," J. Geophys. Res. [Atmos.] **97**(D8), 8047–55 (1992); CA 118 63563m; vertical column abundances.

92WAT J. W. Waters, "Submillimeter-wavelength heterodyne spectroscopy and remote sensisng of the upper atmosphere," Proc. IEEE **80**(11), 1679–701 (1992); CA 118 48565v; detection of ^{79}BrO and ^{81}BrO.

93BRI/VEY I. Bridier, B. Veyret, and R. Lesclaux, "Flash photolysis kinetic study of reactions of the bromine oxide (BrO) radical with BrO and hydrogen dioxide (HO_2) radicals," Chem. Phys. Lett. **201**(5-6), 563–8 (1993); CA 118 90600c; kinetics.

93CUR/RAD J. A. Curry and L. F. Radke, "Possible role of ice crystals in ozone destruction of the lower Arctic atmosphere," Atmos. Environ. Part **27A**(17-18), 2873–8 (1993); CA 120: 139704x; kinetics, reaction in troposphere.

93KUS/SEP R. Kuschel and K. Seppelt, "Bromine bromate, Br_2O_3," Angew. Chem. **105**(11), 1734–5 (1993); Eng. transl., Angew. Chem. Int. Engl. **32**(11), 1632–33 (1993); CA 120 67967k; crystal data.

93MAU/WAH R. L. Mauldin III, A. Wahner and A. R. Ravishankara, "Kinetics and mechanism of the self-reaction of the bromine oxide radical," J. Phys. Chem. **97**(27), 7585–96 (1993); CA 119 81169n; kinetics, an absorption peak of Br_2O_2, formation.

93MON/STI P. S. Monks, L. J. Stief, M. Krauss, S. C. Kuo, and R. B. Klemm," A discharge-flow photoionization mass-spectrometric study of the bromine oxide (BrO)($X^2\Pi$) radical. Photoionization mass spectrum and ionization energy," Chem. Phys. Lett. **211**(4-5), 416–20 (1993); CA 119 169702s; discharge-flow photoionization mass spectroscopy of ^{79}BrO and ^{81}BrO.

93SAL/WOF R. J. Salawitch, S. C. Wofsy, E. W. Gottlieb, L. R. Lait, P. A. Newman, M. R. Schoeberl, M. Lowenstein, J. R. Podolske, S. E. Strahan, *et al.*, "Chemical loss of ozone in the Arctic polar vortex in the winter of 1991-1992," Sci. **261**(5125), 1146–9 (1993); CA 119 185156x; kinetics.

93SCH/ABD L. Schriver-Mazzuoli, O. Abdelaoui, C. Lugez, and A. Scriver, "Matrix reaction of ozone with chlorine and bromine. Fourier transform IR identification of BrClO and ClBrO," Chem. Phys. Lett. **214**(5), 519–26 (1993); CA 120 41778z; IR spectra.

93STI S. Stinson, "New oxides of bromine, nitrogen prepared," Chem. & Eng. News, **51-2** (Nov. 29, 1993); confirms existence of Br_2O_3.

93THO/DAY R. P. Thorn, E. P. Daykin, and P. H. Wine, "Kinetics of the bromine oxide + nitrogen dioxide association reaction. Temperature and pressure dependence in the falloff region," Int. J. Chem. Kinet. **25**(7), 521–37 (1993); CA 119 147452h; kinetics.

93WIN/NIC P. H. Wine, J. M. Nicovich, A. J. Hynes, R. E. Stickel, R. P. Thorn, M. Chian, J. A. Cronkhite, J. C. Shackelford, and Z. Zhao, "Laser flash photolysis studies of atmospheric free radical chemistry using optical diagnostic techniques," SPIE-Int. Opt. Eng. **1715**, 2–14 (1993); CA 119 166708n; kinetics.

94ARP/JOH K. H. Arpag, P. V. Johnston, H. L. Miller, R. W. Sanders and S. Solomon, "Observations of the stratospheric BrO column over Colorado, 40 °N," J. Geophys. Res. [Atmos.] **99**(D4), 8175–81 (1994); CA 121 235108x; UV BrO absorption bands at 349 and 355nm.

94CHI/CAR M. P. Chipperfield, D. Cariolle and P. Simon, "A 3D transport model study of chlorine activation during EASOE," Geophys. Res. Lett. **21**(13), 1467–70 (1994); CA 121 262298r.

94COX/COX J. P. Cox and R. W. D. Cox, "Devolatilizing and stabilizing volatile pollutants using halogen containing treatment agents," PCT Int. Appl. WO 94 14,524, 118 pp. (1994); CA 121 P163030r; reaction.

94DNE/ELI A. S. Dneprovskii, E. V. Eliseenkov and A. V. Podosenin, "Mechanisms of free-radical reactions. XXIX. Free-radical halogenations by chlorine(I) oxide and bromine(I) oxide. Selectivity of haloxy radicals," Zh. Org. Khim. **30**(2), 221–6 (1994); CA 122 9259m; kinetics.

94GAR/SOL R. R. Garcia and S. Solomon, "A new numerical model of the middle atmosphere 2. Ozone and related species," J. Geophys. Res. **99**(D6), 12937–12,951 (1994); CA 121 260161s.

94HAU/PLA M. Hausmann and U. Platt, "Spectroscopic measurement of bromine oxide and ozone in the high Arctic during polar sunrise experiment 1992," J. Geophys. Res. [Atmos.] **99**(D12) 25, 399–413 (1994); CA 122 166007v; detection.

94HJE/ROS A. Hjelmfelt and J. Ross, "Electrochemical experiments on thermodynamics at nonequilibrium steady states," J. Phys. Chem. **98**(39), 9900–2 (1994); CA 121 189795u; reaction.

94INO A. Inoe, "Electrodeless discharge lamps," Jpn. Kokai Tokkyo Koho JP 06.111,790 [94,111,790], 5 pp. (1994); CA 121 P267357u.

94JAC M. E. Jacox, "Vibrational and electronic energy levels of polyatomic transient molecules," J. Phys. Chem. Ref. Data, Monograph No. **3**, 461 pp. (1994); supersedes 84JAC.

94LEO/SEP D. Leopold and K. Seppelt. "Dibromine pentoxide Br_2O_5," Angew. Chem. **33**(9), 975–6 (1994).

94MAR/COR A. Mariani, E. Corpaccioli, M. Fibbi, R. Veratti, A. Hahne, J. Callies and A. Lefebvre, "GOME: a spectrometer for ozone monitoring from space," Proc. SPIE-Int. Soc. Opt. Eng. 2209 (Space Optics 1994: Earth Observation and Astronomy), 57-67 (1994); Ca 122 168487a; detection.

94POM/PIQ J.-P. Pommereau and J. Piquard, "Observations of the vertical distribution of stratospheric OClO," Geophys. Res. Lett. **21**(13), 1231–4 (1994); CA 121 262270a; implication of OClO distribution on spectral observations and reactivity of BrO (which was not observed).

94RAT/JON O. V. Rattigan, R. L. Jones and R. A. Cox, "The visible spectrum of gaseous OBrO," Chem. Phys. Lett. **230**(1-2), 121–6 (1994); CA 122 41328u; visible spectra (gas).

94RUS/BER B. Ruscic and J. Berkowitz, "Experimental determination of ΔH_f^0(HOBr) and ionization potentials (HOBr): implications for corresponding properties HOI," J. Chem. Phys. **101**(9), 7795–7803 (1994); CA 121 308799k.

94THO R. P. Thorn, "Laboratory studies of stratospheric bromine chemistry: kinetics of the reactions of bromine monoxide with nitrogen dioxide and atomic oxygen," 259 pp. (1993); Diss. Abstr. Int. B **54** (12, Pt.1), 6255 (1994); CA 121 138046t.

94TOU R. Toumi, "BrO as a sink for dimethylsulfide in the marine atmosphere," Geophys. Res. Lett. **21**(2), 117–20 (1994); CA 121 87975k.

94WEN/COH P. O. Wennberg, R. C. Cohen, R. M. Stimpfle, J. P. Koplow, J. G. Anderson, R. J. Salawitch, D. W. Fahey, E. L. Woodbridge, E. R. Keim, R. S. Gao, C. R. Webster, R. D. May, D. W. Toohey, L. M. Avallone, M. H. Proffit, M. Loewenstein, J. R. Podolske, K. R. Chan, and S. C. Wofsy, "Removal of stratospheric O_3 by radicals: in situ measurements of OH, HO_2, NO, NO_2, ClO, and BrO," Sci. **266**, 398–404 (1994); CA 121 283972w; kinetics.

95FLE/CHA E. L. Flemings, S. Chandra, C. H. Jackman, D. B. Considine and A. R. Douglass, "The middle atmospheric response to short and long term solar UV variations: analysis of observations and 2D model; results," J. Atmos. Terr. Phys. **57**(4), 333–65 (1995); CA 122 246828b; detection.

95HUE/HAN L. G. Huey, D. R. Hanson and C. J. Howard, "Reactions of SF_6^- and I^- with atmospheric trace gases," J. Phys. Chem. **99**(14), 5001–8 (1995); CA 122 193002w; kinetics.

95HUI/LAS R. Huie and B. Laszlo, "Atmospheric chemistry of iodine compounds," Adv. Chem. Ser., in press.

95LEE T. J. Lee, "Ab initio characterization of triatomic bromine molecules of potential interest in stratospheric chemistry," J. Phys. Chem. **99**, 15074–80 (1995); geometry, enthalpy of formation.

95MAI/BOT G. Maier and A. Bothur, "Bromine superoxide: generation and photoisomerization into bromine dioxide," Z. Anorg. Allg. Chem. **621**, 743–6 (1995); vibrational frequencies.

95MUE/COH H. S. P. Mueller and E. A. Cohen, J. Phys. Chem. (to be published).

95MUE/MIL H. S. P. Mueller, C. Miller and E. A. Cohen, Angew. Chem. (to be published).

95ORL/BUR J. J. Orlando and J. B. Burkholder, ''Gas-phase UV/visible absorption spectra of HOBr and Br_2O,'' J. Phys. Chem. **99**(4), 1143–50 (1995); CA 122 60571j; UV/visible absorption spectra (gas phase).

95THO/CRO R. P. Thorn, J. M. Cronkhite, J. M. Nicovich and P. H. Wine, ''Laser flash photolysis studies of a radical-radical reaction kinetics: $O(^3P_J)$ + BrO reaction,'' J. Chem. Phys. **102**(10), 4131–42 (1995); CA 122 193003x; kinetics.

95THO/MON R. P. Thorn Jr., P. S. Monks, L. J. Stief, S.-C. Kuo, Z. Zhang and R. B. Klemm, (a) 'A preliminary report on the photoionization efficiency spectrum, ionization energy and heat of formation of Br_2O; and the appearance energy of $BrO^+(Br_2O)$,' Brookhaven National Laboratory, Report BNL No. 62126, 11 pp. (1995); (b) 'The photoionization efficiency spectrum, ionization energy and heat of formation of Br_2O,' J. Phys. Chem. (in press).