

NIST-JANAF Thermochemical Tables for the Iodine Oxides

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The thermodynamic and spectroscopic properties of the iodine oxide species have been reviewed. Recommended NIST-JANAF Thermochemical Tables are given for six gaseous iodine oxides: IO, OIO, IOO, IOI, IIO, and IO₃. Sufficient information is not available to generate thermochemical tables for any condensed phase species. Annotated bibliographies (over 400 references) are provided for all neutral iodine oxides which have been reported in the literature. There is a lack of experimental thermodynamic and spectroscopic information for all iodine oxide species, except IO(g) and OIO(g). The recommended thermochemical tables are based on estimates for the structure, vibrational frequencies, and enthalpy of formation based in part on the spectroscopic and thermodynamic data for the other halogen oxides [J. Phys. Chem. Ref. Data **25**, 551 (1996); **25**, 1061 (1996)]. Although there is a definite lack of information in comparison with the other halides, this information is provided for the iodine oxides for the following reasons: (1) to complete the study of the halogen oxide family and (2) to stress the need for additional experimental measurements. Of all the species mentioned in the literature, many have not been isolated or 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: evaluated/recommended data; iodine oxides; literature survey; spectroscopic properties; thermodynamic properties.

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1. Introduction

As a continuation of previous studies which dealt with the thermodynamic properties of the chlorine oxides,¹ oxygen fluorides,² and bromine oxides,³ this study deals with the 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 generate thermochemical tables for iodine oxide species. In general, there are scant data available for the description of the spectroscopic and thermodynamic data for any of the iodine oxides, except for IO(g) and OIO(g). Although the prime emphasis was on the diatomic and triatomic species, a thorough search of all iodine oxygen species was conducted to decide which species had sufficient data. Of the iodine oxides mentioned in the literature, only five have been isolated and (at least, partially) characterized: IO(g), OIO(g), I₂O₄(cr), I₂O₅(cr), I₄O₉(cr).

For the time period 1907–1994, there are only 354 citations in Chemical Abstract Services (CAS) dealing with the iodine oxides; of these, 196 are for I₂O₅ (with the majority of these dealing with commercial applications, as opposed to providing property data) and 73 references deal with IO. Of the approximately 20 oxides mentioned in the literature, however, some do not exist.

Iodine oxides are also of interest due to their involvement in the transport of iodine in a post-accident nuclear environment, while IO is of interest both because of its similarity to ClO (ozone depletion) and as a tropospheric ozone sink. Spectroscopic studies have shown that the ground and first excited electronic states of the halogen monoxides play an intermediate role in the photochemistry of upper atmosphere (e.g., ClO in stratosphere and IO in ionosphere limit the atmospheric abundance of ozone). I₂O₅ is discussed in many articles dealing with the compound's preparation or reaction. Specifically, I₂O₅ has key applications in detecting CO(g). Despite this relevance of the halogen oxides, basic physical properties, in particular the vibrational frequencies and molecular geometries, are poorly characterized.

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 iodine oxides, all such references are provided here. The references were obtained primarily by use of commercial abstracting services and all NIST Data Centers.^a Since the literature survey revealed so few references in total for all iodine oxides, all citations are listed in Sec. 9 (References—Annotated Bibliography), except the approximately fifty patents which are not listed or discussed. It should be noted that

^aChemical 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.

the reading of the individual articles yielded many additional references, most 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 iodine oxide species was in the 1800s. However, these bibliographies are not complete in their coverage for the 1800s. 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 edition (i.e., 1985) of the *JANAF Thermochemical Tables*⁴ does not include any iodine oxygen species, whereas the *Thermodynamic Properties of Individual Substances*⁵ only includes IO(g). This latter critical review referred to data from four spectroscopic studies, three ESR studies, one microwave study, and four dissociation energy studies, the latest of all these citations being dated 1975. The NBS tables⁶ gave information for IO(g) at 298.15 K, for C_p , S , H , and the formation properties, but only an enthalpy of formation for I₂O₅(cr). (Information for four iodine oxide aqueous ions is also included.) Similar information was given in *Thermal Constants of Substances*,⁷ although these authors additionally include an enthalpy of formation of a pentoxide hydrate. (Information for one iodine oxide aqueous ion is included.) These latter two evaluations were performed in 1964 and 1965, respectively, 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 iodine oxides, only IO(g) is listed by NASA–JPL.⁸ 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.*, 1989,⁹ 1992¹⁰). 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.

Iodine and its oxides were reviewed by Roman¹¹ for the Gmelin series. This review covered the literature through 1933 and is an excellent source of information on the oxides for the period of the 1800s. All these references are not included in this article. The Roman review discussed (see pages 432 to 442) the following compounds: I₂O, I₂O₃, I₂O₄ (or IO₂), I₂O₅, I₂O₇, IO₄, I₄O₉, I₁₀O₁₉, and I₆O₁₃. The latter two compounds were stated not to exist. The text discussed the formation and stability of the condensed phase oxides. In general, there were property data presented only for the pentoxide. There was a short mention of the thermodynamic information on the formation of I₂O₅(cr) at the time of this review. There were no experimental studies for the gaseous iodine oxides mentioned.

In a 1963 review article, Schmeisser and Brandle¹² summarized the data pertaining to the properties and chemistry of the halogen–oxygen compounds. Although these authors did not specifically discuss IO, they highlighted the fact that

only I_2O_5 was well defined with only two other oxides having been isolated, but not unequivocally characterized— I_2O_4 and I_4O_9 . A 1968 article by Selte and Kjekshus¹³ stated that two oxides I_2O_4 and I_2O_5 were properly established whereas the rest have a high degree of uncertainty associated with them. In a 1972 review of the halogen oxides, Brisdon¹⁴ discussed seven iodine oxide species: IO, IO_2 , IOO, IO_3 , IO_4 , I_2O_4 , and I_2O_5 . Whereas there was a spectroscopic characterization given for IO, there was only structural information in the condensed phase given for I_2O_4 and I_2O_5 . IO_2 and IO_3 were mentioned only in terms of their presumed formation in iodate solutions. A later review (1980) by Wikjord *et al.*¹⁵ suggested that I_2O_4 , I_2O_5 , and I_4O_9 have been isolated and fully characterized, crystallographically.

In 1977, Clyne and Curran¹⁶ surveyed the 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. The authors stated that so far no systematic kinetic studies of IO had been performed.

(After this article was written and reviewed, we became aware of the existence of another review article by Wayne *et al.*¹⁷ 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 iodine oxide compounds is questionable. The thermal instability of the iodine oxides has led to numerous difficulties in characterizing specific iodine 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: IO; IO_2
 Postulated: IOO; $IO_{2,24}$; IO_3 ; IO_4 ; I_2O ; I_2O_2 ; I_2O_8
 Hypothetical molecule to describe ternary systems: I_2O_7
 Observed as crystalline solid: I_2O_4 ; I_2O_5 ; I_2O_6 ; I_4O_9
 No conclusive confirmation as to existence: I_2O_3 ;
 I_6O_{13} ; $I_{10}O_{19}$

In the following discussions, analyses and calculations, the 1993 atomic weights of the elements are used:¹⁸ $A_r(I) = 126.904 47 \pm 0.000 03$; $A_r(O) = 15.999 4 \pm 0.000 3$ are used. Since the mid-1950s, the relative atomic weight of oxygen has changed by 0.0006 to 15.9994. Similarly for iodine, the relative atomic weight has changed by 0.005 53 to 126.904 47. However, since 1961 the change has been 0.0003. 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:¹⁹ $R = 8.314 510 \pm 0.000 070 \text{ J K}^{-1} \cdot \text{mol}^{-1}$. In comparison to the 1973 fundamental constants (16), R has changed by $+0.0001 \text{ J K}^{-1} \cdot \text{mol}^{-1}$.

SI units are used for the final recommendations. Since we are dealing only with spectroscopic information, the resulting calculated thermodynamic tables will refer to thermody-

amic 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 $\Delta_f H^\circ$ 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 monoatomic and diatomic iodine and oxygen. These latter reference state thermochemical tables, as originally calculated, were based on the 1973 fundamental constants²⁰ and the 1981 relative atomic weights.²¹ This will cause a slight offset in the formation properties of the order 0.01 kJ mol^{-1} at most; such an offset is still outside the uncertainty range of the enthalpy of formation of the iodine oxides. Neumann²² has presented an identical thermodynamic table for IO(g); this table was prepared jointly with this author.

1.1 References for Introduction

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2. Chemical Species Coverage

The following is a list of all iodine oxide species cited in the Chemical Abstracts Services (CAS) Indices (formula and substance). Aqueous ions and positive/negative 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). Numerous citations, covering 1995–1996 are included, but the coverage may not be complete. It is important to note that this listing includes species which now are known not to exist, but they were cited in the early literature. Deleted CAS Registry Numbers are given to assure the reader that all past citations were retrieved. There are difficulties in discussing "a" oxide such as IO_2 in which references are made to IO_2 and I_2O_4 as the same compound. Similar problems exist with IO_3/I_2O_6 and IO_4/I_2O_8 . There is not sufficient experimental information to confirm the existence of six of the listed oxides (I_2O , I_2O_2 , I_2O_3 , I_2O_7 , I_6O_{13} , and $I_{10}O_{19}$). In addition, there are no experimental data on the gaseous radicals IO_3 and IO_4 . Many of the reported species have been proposed in reaction schemes, but not characterized. Also, it is important to note that there is no information available to suggest the existence of asymmetric isomers of the triatomic species IOO and IIO , although the former has been proposed in a kinetic scheme. Such asymmetric isomers exist for the chlorine, fluorine, and bromine oxides.

Iodine oxide species

Formula ^a	Name	Chemical Abstracts Registry Numbers	
		Deleted No.	Current No. ^d
IO (IO)	Iodine oxide	50400-00-5	14696-98-1
IO_2 (OIO)	Iodyl	...	71132-73-5
IO_2 (OIO)	Iodine oxide	...	13494-92-3
$I^{17}O_2$	Iodyl- $^{17}O_2$...	116854-14-9
IO_2 (IOO ^b)
$IO_{2.24}$	Iodine oxide	...	108216-85-9
IO_3 (pyr.)	Iodine oxide	...	13870-16-1
IO_4	Iodine oxide	...	11074-36-5
I_2O	Iodine oxide	...	39319-71-6
I_2O_2	Iodine oxide
I_2O_3	Iodine oxide	...	11085-17-9
I_2O_4	Iodine oxide	12399-08-5 ^c	...
I_2O_5 ($O_2I-O-IO_2$)	Iodine oxide	7790-35-4	12029-98-0
I_2O_6	Iodine oxide	64052-04-6 ^c	...
I_2O_6 ($IO_2^+IO_4^-$)	Iododioxxygen periodate	...	65355-99-9
I_2O_6 ($O_2I^+-OIO_3^-$)	Iodyl periodate	...	63912-61-8
I_2O_7	Iodine oxide	20270-38-6	12055-74-2
I_2O_8 ($O_3I-O_2-IO_3$)	Iodine oxide	...	81756-07-2
I_4O_9 [$I(O_3)_3$]	Iodine iodate	73560-00-6	66523-94-2
I_6O_{13}	Iodine oxide
$I_{10}O_{19}$	Iodine oxide

^aThe second 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.

^bArticles exist which refer to this species, but there are no definitive data to prove its existence.

^cIn those cases where a deleted CAS Registry Number exists, but no current CAS Registry Number exists, the species has been reassigned to another CAS Registry Number. This is discussed in a later section.

^dIf no CAS Registry Number appears in this column, then the species is assumed NOT to exist or no characterization has been made.

3. Historical Perspective of the Iodine Oxide Studies

It is informative to briefly summarize the types of studies which have been conducted through the years on the iodine oxides. Specific references are given in Sec. 9. This section is intended to simply highlight developments through the years.

Using the CAS Collective Indices as a backdrop for these introductory comments, the period of 1907 to 1926 (the First and Second Collective Indices) reveals no information as to the thermodynamic and spectroscopic properties of any iodine oxides. For this time period, there are twelve citations (of which nine are for I_2O_5); some of these articles refer to additional work in this time period (although not noted by CAS) as well as earlier work. The retrieved information suggests that the preparation and identification of the various condensed phase oxides were still in their infancy. For example, there are articles which suggest that the earlier identification (pre-1907) of the oxides I_6O_{13} and $I_{10}O_{19}$ was incorrect and that the oxide was in fact I_2O_4 which was (at that time) called, iodine iodate ($IO \cdot IO_3$). Another article suggested that it was not clear as to whether the molecular spe-

cies was IO_2 or I_2O_4 . In any event, there is information on the preparation, existence (or lack thereof), and reactivity of four iodine oxides (all in the condensed or aqueous phase)— I_2O_4 , I_2O_5 , I_6O_{13} , and $\text{I}_{10}\text{O}_{19}$ —but not any spectroscopic and thermodynamic data. Of the nine pentoxide articles, four deal with preparative techniques and two with thermal stability.

From 1927 to 1946 (the Third and Fourth Collective Indices), there is continued activity in the preparation of various iodine oxides (only in the condensed or aqueous phase). Three articles involve the preparation of lower oxides (I_2O_3 and I_2O_4) and their relationship to I_2O_5 . The remaining 25 citations deal with the pentoxide. There is considerable effort in reaction schemes involving the preparation and identification of the pentoxide and its hydrates. Articles on density and diamagnetism (structure) are the first citations on the properties of the pentoxide. Thermal decomposition (to the elements) studies suggest that decomposition "point" is 275 °C.

For the time period 1947 to 1961 (the Fifth and Sixth Collective Indices), $\text{IO}(\text{g})$ has now been detected in flames and preliminary spectroscopic data were recorded yielding dissociation energy and rotation-vibration information. Of the 41 citations in this period, 23 deal with the pentoxide, with most of these involving commercial applications. However, some articles report the IR spectrum and structure of the condensed phase of the tetroxide and pentoxide.

In the time period 1962 to 1971 (the Seventh and Eighth Collective Indices), there are 87 references of which 44 refer to the pentoxide. Additional information on the spectroscopic properties of $\text{IO}(\text{g})$ was published. The first calculational information on the vibrational behavior of $\text{IO}_3(\text{g})$ appeared, as well as three articles dealing with the structure and spectra of I_2O_4 in the condensed phase. Although the majority of the pentoxide references deal with reactions and commercial applications, there are four articles which deal with the structure and spectra. No experimental information on the enthalpy of formation has appeared for any of the oxides except $\text{IO}(\text{g})$ and some pre-1900 studies of I_2O_5 .

Of the 95 articles which are reported in the literature for the time period 1972 to 1981 (the Ninth and Tenth Collective Indices), the majority of the articles deal with $\text{IO}(\text{g})$ and $\text{I}_2\text{O}_5(\text{cr})$. There are numerous spectroscopic and dissociation energy studies on the monoxide. The pentoxide work was heavy on applications, including many patents, although there was continued examination of the relative stability among condensed phase oxides. There were also calculations and estimations involving $\text{IO}(\text{g})$, but no experimental studies.

In the time period 1982 to 1991 (the Eleventh and Twelfth Collective Indices), the literature deals primarily (again) with $\text{IO}(\text{g})$ and $\text{I}_2\text{O}_5(\text{cr})$. The pentoxide studies deal mostly with reactions and applications, with no definitive property characterization. Even the work involving $\text{IO}(\text{g})$ was related more to reactions, rather than spectroscopic and thermodynamic determinations.

In summary, there are no heat capacity, enthalpy, or vapor pressure studies for any of the iodine oxides, with the excep-

tion of one sublimation study for I_2O_5 . There are many articles which detail the preparation and decomposition temperature of various crystalline oxides. There are some early (pre-1900) enthalpy of formation data for $\text{I}_2\text{O}_5(\text{cr})$. The spectroscopic properties and dissociation energy for $\text{IO}(\text{g})$ have been studied adequately, but the complete spectroscopic determination and enthalpy of formation values for any of the other iodine oxides are lacking. For the iodine oxides, many vibrational frequencies have been determined for the crystalline phase but none for the gas phase except IO_2 . In addition, only IO and IO_2 have been studied in the gas phase. There are some experimental studies in a solution or a matrix.

4. Summary of the Data for the Iodine 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 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 iodine oxides in the condensed phase. However, relying on information from the fluorine, chlorine, and bromine oxides, estimates can be made for the structure and spectroscopic properties of $\text{IO}_2(\text{g})$ and $\text{I}_2\text{O}(\text{g})$, as well as for the asymmetric isomer.

For the diatomic molecules, spectroscopic information on the electronic energy levels and vibrational-rotational structure is necessary. Experimental data of this type are available for $\text{IO}(\text{g})$. Similar information on ClO and BrO is available for comparison.

4.2 Thermodynamic Information

The literature survey revealed little or no information on the thermodynamic properties of any of the iodine oxides, except for $\text{IO}(\text{g})$, which was derived from spectroscopic data. Although not explicitly cited in Chemical Abstracts, there is a reference for the enthalpy of formation for $\text{IO}_3(\text{g})$ and $\text{I}_2\text{O}_5(\text{cr})$. There are, however, numerous citations as to the thermal stability of the various condensed phase oxides.

There are insufficient data available to permit the calculation of thermodynamic functions for the condensed phase of any of the iodine oxides. No heat capacity or enthalpy data are reported in the literature for any of these oxides. There are also no data for the melting of the various condensed phase. Limited stability information is available which refers to the decomposition of I_2O_4 , I_2O_5 , and I_4O_9 . Melting, if observed, is in combination with decomposition.

For the gas phase species, only IO(g) has dissociation energy information available so that an enthalpy of formation may be calculated. No experimental formation information has been reported in the literature for any of the other iodine oxides.

5. Discussion of Literature Data

The information is discussed in terms of the individual iodine oxide species. All species cited in the Chemical Abstracts formula and substance index are discussed as well as those additional species which are mentioned in the individual articles. This is not to imply that all those species exist or have been isolated and characterized. For example, I₆O₁₃ and I₁₀O₁₉ do not exist, whereas I₂O₃ and I₂O₇, although discussed in many articles, have never been isolated. The references for each of the following subsections are found in the corresponding subsection of References—Annotated Bibliography (Sec. 9).

5.1 IO

There is a discontinued CA Registry Number 50400-00-5 that presumably referred to an unspecified iodine oxide compound, in which the iodine to oxide ratio was one to one.

The reported references for IO(g) may be arbitrarily categorized as follows:

1. Spectra (see Table 3)
 - [37VAI], [46BLA/IRE], [48COL/GAY], [50HER], [58DUR/RAM], [60DAS/WAD], [60DUR/LEG], [72YAN], [73KAP], [73SAI], [79HUB/HER], [80LOE/MIL], [83BEK/MEE], [83ENG/TAL], [84BUR/LAW], [91GIL/POL], [92GIL/POL]
2. Preparation/formation/reaction (see Tables 1a, 1b, 2)
 - [60DAS/WAD], [62GUR/KHA], [69HAT/HUS], [73PAR/HER], [82ANT], [82FUR/NUO], [80BAR/BEC], [85BUX/KIL], [90BRA/DOR], [90BUB/LAR], [90DAY/WYN], [90DAY/WIN2], [90VOH/BAD], [92BUB/LAR], [92DUB/SKU], [92HEL/FOG]
3. Dissociation energy (see Table 4)
 - [50HER], [53GAY], [54COT], [58BRE], [58DUR/RAM], [61LIP/STE], [61PHI/SUG], [62GUR/KHA], [63SCH], [65SIN/RAI], [66VED/GUR], [68WAG/EVA], [69BRE/ROS], [69HER/HUI], [70CLY/CRU], [70DAR], [72RAI/SHA], [72TRI/GOH], [74RAO/RAO], [75RAD/WHI], [77GLI], [79ADD/DON], [79HUB/HER], [80KER/TRO], [82BAU/COX], [83BUS/SIB], [88TYK], [89GUR/VEY], [89RED/RAO], [92MAG/LAV], [94RUS/BER], [95HUI/LAS], [95ZHA/MON], [96GIL/TUR]
4. EPR (see Table 3)
 - [67CAR/DYE], [67CAR/CUR], [69CAR], [70CAR/DYE], [71BYF/CAR], [71MIL], [72BRO/BYF]
5. Radiolysis/photolysis

[61MCK/NOR], [63BUR/NOR], [70AMI/TRE], [70AMI/TRE2], [73STU/TEZ], [76CAL/MET], [77ANT/BUR], [77CAL/MET], [83COX/COK], [83INO/SUZ], [85BUX/SEL], [92KAR/END]

6. Kinetics

[67MCE/PHI], [69HER/HUI], [70CLY/CRU], [75CLY/WAT], [75RAD/WHI], [75RAD/WHI2], [77CLY/CUR], [79ADD/DON], [79BRU/FIE], [79GOR/NOV], [79GOR/NOV2], [80KER/TRO], [81GAR/WAT], [81RAY/WAT], [82BAU/COX], [83BUS/SIB], [83THO/ZAF], [85JEN/COX], [86SAN], [87BAR/BEC], [87ELO/RYN], [87MAR/JOH], [87MAR/JOH2], [88COS/TEN], [88STI/HYN], [90BAR/BAS], [91BAR/BAS], [91JEN/COX], [91MAG/MEL], [92MAG/LAV], [92WHI/SMI], [95TUR/GIL]

7. Other

[67STU/HUS], [69BRE/ROS], [71KAU/KOL], [74DHA/CLE], [74DHA/CLE2], [74SCH], [76REF/FRA], [76REF/FRA2], [77VOG/DRE], [77VOG/MIS], [81GRO/LAU], [81SEH/SUT], [82GAR], [84SAU/TAT], [87KAR], [92GIL/POL], [94SOL/GAR]

Fortunately, there is sufficient information on the spectroscopic properties (including a rotational-vibrational analysis) of IO(g) to characterize the thermodynamic properties of this chemical species. The results are in reasonable agreement with the results of the other halogen monoxides. It is not the intent of this article to discuss the articles dealing with formation, reaction and kinetics.

Durie *et al.* [60DUR/LEG] photographed the methyl iodide flame bands lying in the region 4100–6300 Å. These bands are attributed to the $A^2\Pi-X^2\Pi$ transition of the IO molecule. A rotational and vibrational analysis was carried out to provide the molecular constants for the $X^2\Pi_{3/2}$ and $A^2\Pi_{3/2}$ states. This paper builds on and extends the earlier observations and analyses of [37VAI], [48COL/GAY], and [58DUR/RAM]. Blake and Iredale [46BLA/IRE] published a revised analysis of portions of the [37VAI] data. Coleman *et al.* [48COL/GAY] stated that this led to an unsatisfactory intensity distribution. Thus, [48COL/GAY] remeasured the bands and extended the system to larger wavelengths. Durie and Ramsay [58DUR/RAM] measured the absorption spectra of IO and derived a vibrational analysis consistent with Coleman *et al.* [48COL/GAY]. Engleman *et al.* [83ENG/PAL] observed an absorption spectrum of I¹⁸O which was in agreement with that predicted by [60DUR/LEG]. This spectrum was recorded as part of a high temperature spectra of a quartz cell containing an I₂-O₂ mixture. The recommended spectroscopic information for the X and A states is very similar to that recommended by Huber and Herzberg [79HUB/HER]. These authors relied on the experimental data of [48COL/GAY], [58DUR/RAM], and [60DUR/LEG]. The earlier review by Herzberg [50HER] was based on the data of [46BLA/IRE], [48COL/GAY], and [37VAI] and is superseded by [79HUB/HER].

Information published since these reviews provided more definitive vibration and rotation constants [83BEK/MEE].

Using a high resolution laser-rf spectroscopy on the $A^2\Pi_{3/2}-X^2\Pi_{3/2}$ system of iodine oxide, the vibrational and rotational constants for the ground state have been refined from those previously recommended by Durie *et al.* [60DUR/LEG].

The ground state configuration, $X^2\Pi_{3/2}$ (inverted doublet), was confirmed by the EPR measurements of [70CAR/DYE] and [72BRO/BYF]. [70CAR/DYE] determined the fine structure splitting to be $A = -446 \pm 70 \text{ cm}^{-1}$, although they questioned the validity of this value and felt that independent determinations should be made. Brown *et al.* [72BRO/BYF] also used ESR techniques to determine the spin-orbit coupling constant A and the ground electronic state. The authors derived $A = -2330 \pm 230 \text{ cm}^{-1}$. Both studies indicated that the value of A was suspect and should be of the order of 1000 cm^{-1} .

Gilles *et al.* [91GIL/POL] used photoelectron spectroscopy to obtain the spectra for $\text{IO}(^2\Pi_{3/2}, ^2\Pi_{1/2}; \nu') + e^- \leftarrow \text{IO}^-(^1\Sigma^+; \nu'')$. This measurement provided direct structure information on $\text{IO}^-(g)$ and reported the first observation of the ground state $^2\Pi_{3/2}-^2\Pi_{1/2}$ spin-orbit splitting for IO. The authors observed two vibrational progressions separated by $2091(40) \text{ cm}^{-1}$ which they attributed to the spin-orbit components of the IO ground state. In their analysis of the data, the authors adopted the r_e , ω_e , $\omega_e x_e$ values from [83BEK/MEE] and derived the values for these three parameters in the $X^2\Pi_{1/2}$ component. This work was continued and further discussed in [92GIL/POL]. We recommend an excited state at 22469.8 cm^{-1} based on the values from [83BEK/MEE].

The dissociation energy has been calculated by many different techniques. The various studies have not improved the reliability of the dissociation energy. These values are summarized in Table 4. The derived values range from 176 to 249 kJ/mol, as referenced in Table 4. The values may be grouped into two types: (1) derived from a treatment of the observed vibrational energy levels and (2) extracted from kinetic studies. The largest value is derived from the curve fitting approach of [89RED/RAO], using a three-parameter modified Lippencott potential function (based on the spectroscopic data of [83BEK/MEE]).

Coleman *et al.* [48COL/GAY], from their study of the IO spectrum in flames, used a graphical Birge-Sponer technique to give $1.9 \pm 0.2 \text{ eV}$ (44 kcal/mol). Durie and Ramsay [58DUR/RAM] stated that since only six bands were observed in their study of the absorption spectrum of IO, it was not possible to obtain an accurate value for the dissociation energy of the ground state. They derived an upper limit from the observed predissociation. Thus, they calculated a value $< 21\,976 \text{ cm}^{-1}$ (62.8 kcal/mol or 2.72 eV). However, Durie and Ramsay felt that a better estimate could be obtained from a Birge-Sponer extrapolation of the first four vibrational levels in the upper state. This led to $10\,200 \text{ cm}^{-1}$. However, since the accepted values (at that time, 1958) for ClO and BrO were approximately 10% less than the values calculated by the same procedure, they applied the same correction to IO and calculated $14\,800 \pm 1800 \text{ cm}^{-1}$ (42 ± 5

kcal/mol or $1.8 \pm 0.2 \text{ eV}$). Subsequent work by Durie, which led to vibrational constants with greater precision, would not lead to any improvement in the calculation of the dissociation energy due to considerable extrapolation.

Using flame photometry, Phillips and Sugden [61PHI/SUG] measured the intensity of the (0,4) band of IO at 5307 \AA to determine the temperature dependent (1900–2700 K) equilibrium constant for the dissociation energy of IO. They determined a value of $57 \pm 6 \text{ kcal/mol}$ at 0 K. This value was calculated from the assumed enthalpy of formation value of 63 kcal/mol at 2000 K. This value is considerably higher than the earlier determined values. Herron and Huie [69HER/HUI], in their study of the rate constants of atomic oxygen with chloroalkanes and bromoalkanes, stated that the bond dissociation of IO ($238 \pm 24 \text{ kJ mol}^{-1}$), as derived from [61PHI/SUG], is the value which is compatible with their iodine atom abstraction mechanism. The value from the [58DUR/RAM] study was too small.

Singh and Rai [65SIN/RAI] calculated RKR potential energy curves for the $X^2\Pi$ and $A^2\Pi$ states of IO. The spectroscopic data used as the basis for this calculation were those of Durie *et al.* [60DUR/LEG] and Durie and Ramsay [58DUR/RAM]. Using the three-parameter Lippencott function to calculate the dissociation energy from the potential energy curve, the authors arrived at $20\,000 \text{ cm}^{-1}$. This is compared with an earlier reported value of $1.9 \pm 0.2 \text{ eV}$, which undoubtedly is the value of Coleman *et al.*

A least-squares fitting of the RKR curve with the Hulbert-Hirshfelder formation gave a dissociation energy value of 1.94 eV [72TRI/GOH]. The authors stated that the three-parameter Lippencott potential function fails to reproduce the experimental potential energy curve in the case of IO.

Rao, Rao, and Rao [74RAO/RAO] estimated the dissociation energy of the upper state of IO, the A state, by fitting an empirical potential energy curve from Lippencott's three-parameter function and the Hulbert-Hirshfelder function with the true potential energy curve. They determined the value 1.425 eV for the upper state and confirmed the value of Trivedi and Gohel, that is, 1.94 eV for the ground state. This value was also supported by fitting an electronegativity function suggested by Szoke and Baitz. As mentioned earlier, [89RED/RAO], using a three-parameter modified Lippencott potential function, based on the spectroscopic data of [83BEK/MEE], calculated a dissociation energy of 59.6 kcal/mol . However, recall [72TRI/GOH] claimed this technique was not acceptable as stated earlier.

Baulch *et al.* [82BAU/COX] listed a dissociation value of $184 \pm 21 \text{ kJ/mol}$ as given by [80KER/TRO].

Maguin *et al.* [92MAG/LAV], in studying the kinetics of the reactions of IO radicals with NO_2 and HO_2 , reported three enthalpy of formation values for IO. They referred to $\Delta_f H(\text{IO}, 298 \text{ K}) = 172 \text{ kJ/mol}$ from [90DEM/MOL], 132 kJ/mol from [89GUR/VEY], and 107 kJ/mol from [89RED/RAO]. Although these authors did not recommend a specific value for $\Delta_f H$, they implied that the latter value from [89RED/RAO] was not consistent with their kinetic observations.

Herron and Huie [69HER/HUI] and Huie and Laszlo [95HUI/LAS], in their kinetic studies, have questioned the validity of the spectroscopically derived dissociation energy values. Whereas [69HER/HUI] preferred the results of [61PHI/SUG], Huie and Laszlo [95HUI/LAS] have adopted an enthalpy of formation value of 130 kJ/mol based on the molecular beam studies of [75RAD/WHI] and [83BUS/SIB] (refer to Table 4).

The recommended thermodynamic properties of IO(g) by Wagman *et al.* [82WAG/EVA] were based on the spectroscopic measurements of Durie and Ramsay [58DUR/RAM] and Durie, Legay, and Ramsay [60DUR/LEG]. The corresponding publication by Glushko and Medvedev [65GLU/MED] based their recommended thermal function values on the earlier interpretation by Gurvich *et al.* (1962) and the dissociation energy value on the results of Coleman, Gaydon, and Vaidya (1948), Durie and Ramsay (1958), and Phillips and Sugden (1961). The more recent analysis of Gurvich *et al.* [62GUR/KHA] relied on the results of Vaidya (1937), Blake and Iredale (1946), Coleman, Gaydon, and Vaidya (1948), Durie and Ramsay (1958), and Durie, Legay, and Ramsay (1960). The recommended spectroscopic information given by Huber and Herzberg [79HUB/HER] was based on the data of Coleman *et al.* (1948), Durie and Ramsay (1958), and Durie *et al.* (1960). The thermochemical table of Brewer and Rosenblatt [69BRE/ROS] is based on the earlier vibrational and rotational constants data of Durie *et al.* (1960) and the energy level values of Durie *et al.* (1960), Moore (1958), and Herzberg (1950). The recommended dissociation value of 46 ± 7 kcal was based on the results of Coleman *et al.* (1948), Durie and Ramsay (1958), and Phillips and Sugden (1961).

5.2 IO₂

The articles dealing with IO₂ can be classified as follows. Of prime importance to this article are the spectroscopic and properties studies.

1. Radiolysis/photolysis
[69BAR/GIL], [70AMI/TRE], [70AMI/TRE2],
[72BAR/GIL], [73TEN/FAR], [86BYB], [89SAG],
[92KAR/END]
2. Reactions
[09MUI], [64GIL/SEN]
3. Intermediates
[61PAV/RAF], [80COO], [82FUR/NOY],
[82FUR/NOY2]
4. Spectroscopy/structure
[60DAS/WAD], [60DUV/LEC], [81ELL/WOL],
[92GIL/POL]
5. Preparation/formation
[1844.IL], [60DAS/WAD], [80WIK/TAY]
7. Properties
[67STU/HUS], [80WIK/TAY], [81ATH/MOR],
[86BYB], [88BYB], [92GIL/POL], [94FJE/KJE]

There is only one reported study involving this oxide in the gas phase [92GIL/POL], but there is no experimental

structural or enthalpy of formation information. Most citations deal with the assumed existence in an aqueous or matrix media.

CA Registry Number 116854-14-9 corresponds to the isotope ¹⁷O₂ (one reference which deals with ESR spectrum [88BYB]). The author measured the ESR spectra of this diiodide embedded in KClO₄. From the complicated ¹⁷O hyperfine structure, he determined the hyperfine and quadrupole tensors of ¹⁷O. Byberg [88BYB] stated that the ground state of the free IO₂ molecule belonged to the representation B₁ of the point group C_{2v}. The author assumed the bond angle of OIO to be 118°. The analysis of the ¹⁷O hyperfine patterns of ¹⁷O₂ supported the earlier conclusion that the electronic properties closely resemble those of ClO₂ and BrO₂.

An EPR study [81ATH/MOR] suggests that IO₂ in a γ -irradiated KIO₂F₂ crystal is a bent symmetric radical, OIO, as are the chlorine and bromine counterparts in comparable studies.

An ESR spectrum of IO₂ was obtained from the selective photolysis at room temperature of IO₄⁻ embedded in KClO₄ crystals and the subsequent x irradiation at low temperatures [86BYB]. The author's conclusion was that the C_{2v} nuclear geometry of IO₂ in KClO₄ resembles that of ClO₂ in the gas phase. Thus, the bond length of IO₂, 1.815 Å, was taken as that of ClO₂ (1.475 Å), corrected for the difference between the covalent radii of chlorine and iodine (0.34 Å). However, the bond angle of IO₂ in this lattice could be significantly smaller than that of ClO₂, 117.6°.

Gilles *et al.* [92GIL/POL] measured the photoelectron spectra of OIO⁻(g). In addition to deriving the electron affinity of OIO, the authors determined two vibrational frequencies [the symmetric stretch (765 cm⁻¹) and bend (192 cm⁻¹)]. The structure of the molecule was not determined, but was assumed to be of C_{2v} symmetry.

Numerous other studies involve the kinetic description of the formation and decay of this transient species in aqueous medium, as well as reactions involving IO₂ as an intermediate.

A confusing aspect for this chemical species involves the condensed phase characterization: is the "molecule" IO₂ or I₂O₄? The Chemical Abstracts literature references for IO₂ include I₂O₄ references. The early references for the dioxide are in fact for the tetroxide. There are two citations for IO₂ which deal with the crystal structure of I₂O₄. Indications are that the structure of the species in the condensed phase is perhaps IO · IO₃. The most recent reference to this species is a crystal structure study of I₂O₄ in which it was concluded that a chain structure exists: (····-I-O-IO₂-O····).

5.3 Iodyl—IO₂

Iodyl (CA Registry Number 71132-73-5), with a structure OIO, has one reference reported in CA. This reference [79BRU/FIE] does not appear to give any additional structural information other than that which is provided in the other articles dealing with IO₂. Brummer and Field reported

on the oxidation of Fe(II) to Fe(III) by IO_3^- in strongly acidic aqueous media. IO and IO_2 are among the seven proposed reactive intermediates.

5.4 IOO

There are three references which propose this species as an intermediate in aqueous reaction schemes [70CLY/CRU, 77CLY/CUR, 80COO]. This species has not been isolated or characterized.

The thermodynamic properties of IOO(g) could be estimated in comparison with the properties of FOO and ClOO, both of which were well characterized. Unfortunately, BrOO is not well characterized.

5.5 $\text{IO}_{2.24}$

There is only one reference to this species in which its formation in the reaction of iodine with ozone is discussed [80VIK/TOR].

5.6 IO_3

The articles dealing with IO_3 can be classified as follows. Of prime importance to this article are the spectroscopic and enthalpy of formation studies.

1. Enthalpy of formation
[48FAR/KLE]
2. Vibrational frequencies/structure
[56VEN/SUN], [63VEN/RAJ], [64RAO/SAN],
[72RAO], [78THI/MOH]
3. Formation/preparation
[1861KAE], [58ODE], [59HAU], [63PAC/HAU],
[68SEL/KJE], [77SEI/WEI], [86VIK/TOR]
4. Related spectra
[60DAS/WAD], [77SIE/WEI]
5. Intermediate
[61PAV/RAF], [82NOS/NOS]
6. Photolysis/radiolysis
[69BAR/GIL], [70AMI/TRE], [70AMI/TRE2],
[72BAR/GIL], [73TEN/FAR], [81KLA/SEH],
[82WAG/STR], [85BUX/SEL]

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 -28 kcal/mol. Although the authors, Farkas and Klein, stated that they calculated the enthalpy of formation of IO_3 , the formula given is IO_3^- .

There are five references of a theoretical nature which deal specifically with the structure and spectroscopic properties of the gaseous trioxide. Unfortunately, there are no experimental studies involving the radical in the gas phase.

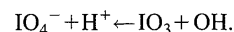
The spectroscopic articles for the gas phase radical involve force field calculations of pyramidal XY_3 type molecules [56VEN/SUN, 63VEN/RAJ, 64RAO/SAN, 72RAO, 78THI/MOH]. Contrary to the implications of these five articles, there is no observed structural information nor is there any observed vibrational information. Upon examination of the

earlier literature cited by these authors, vibrational frequency information was found for IO_3^- in a crystalline environment. Two of the four vibrational frequencies matched exactly with those reported for IO_3^- . These articles have assumed a pyramidal structure with a O-I-O angle of 89° (same angle was used for the chlorine, bromine, and iodine trioxides); a bond distance I-O of 1.79 \AA (from Badger's rule), and vibrational frequencies (in cm^{-1}) of $\nu_1=780 [A_1]$, $\nu_2=357 [A_2]$, $\nu_3=809 [E]$, and $\nu_4=326 [E]$. Unfortunately, ν_4 is reported as 326 cm^{-1} by Venkateswarlu and Sundaram [56VEN/SUN] and as 362 cm^{-1} by Thirugnanasambandam and Mohan [78THI/MOH]. From an examination of the calculations and the trends in the series of the three halogen trioxides, it is apparent that the frequency should be 326 cm^{-1} .

Many other references deal with (1) the thermal decomposition of orthoperiodic acid [59HAU, 63PAC/HAU] and NH_4IO_3 [61PAV/RAF], (2) the existence of solid I_2O_6 (not IO_3) and its Raman spectra [77SIE/WEI], (3) infrared and visible spectra of IO_3^- [60DAS/WAD], and (4) numerous articles on the production of the transient radical in an aqueous medium through flash photolysis and pulse radiolysis of aqueous iodate solutions. The emphasis in these latter type articles is the explanation of the chemistry through a kinetic interpretation.

Farkas and Klein [48FAR/KLE] studied the decomposition of bromate ion in aqueous solution. IO_3 was proposed as an intermediate to describe the kinetics of the decomposition process.

There are three flash photolysis studies of periodate solutions by Barat and Gilles [72BAR/GIL], Klaning and Sehested [81KLA/SEH], and Wagner and Strehlow [82WAG/STR]. Barat assumes the radical IO_4 is an intermediate whereas Klaning assumes IO_3 and an unspecified I(VIII) species are intermediates. In Wagner and Strehlow, the increase in the resistance of the solution during the flash was attributed to the reaction



Two methods proposed for the elimination of the radical were the dimerization to I_2O_6 and the reaction with ozone to yield IO_4 .

5.7 IO_4

There are no reported studies involving this oxide in the gas phase: i.e., there is no experimental structural, vibrational frequency or enthalpy of formation information. A CA Registry Number exists for IO_4 , but the structure is not determined. The existence of the IO_4 radical had been "established" as a short lived species by Gomberg as early as 1923 [23GOM]. Selte and Kjekshus [68SEL/KJE], in their study of the $\text{H}_2\text{O}-\text{I}_2\text{O}_5$ system, questioned the existence of IO_4 .

There are four recent references which discuss the existence of the IO_4 radical. They all involve the existence of this radical in an aqueous medium, not in the gas phase. The studies involve the pulsed radiolysis [71LES/BAR], flash

photolysis [82WAG/STR], laser flash photolysis and pulsed radiolysis [81KLA/SEH], and radiation induced redox [85BUX/SEL] of aqueous periodate solutions. Neither study reports any information as to the structure of the radical, its vibrational frequencies, or its enthalpy of formation. Thermal functions for this radical cannot be reliably estimated since there are no related substantial data for the other halogen oxides $XO_4(g)$.

Lesigne *et al.* [71LES/BAR] studied the IO_4^{-2} aqueous ions and IO_4 radicals formed by the pulse radiolysis of periodate ion in aqueous medium. The authors state that they also observed this transient species by flash photolysis of deaerated periodate solution.

Ten years later, Wagner and Strehlow [82WAG/STR] studied the flash photolysis of periodate in the pH range 2.44 to 4.99 in which three reactions were observed. In this experimentation, the authors discuss the formation of the IO_4 radical and its dimerization to I_2O_8 and the related kinetics.

Klaning *et al.* [81KLA/SEH] also used flash photolysis to study periodate solutions. They assumed the formation of IO_3 and an unspecified I(VIII) species.

Buxton and Sellers [85BUX/SEL] proposed the formation of IO_4 as an intermediate species in the pulsed radiolysis of aqueous periodate solutions.

5.8 I_2O

There is no thermodynamic or spectroscopic information available for this chemical species. Most of the reported information deals with the reactivity of this oxide as an intermediate in various reactions; [38MAS], [72FOR/GOO], [76CAM/HAY], [82NOS/NOS]. There are two articles from which spectroscopic information might be extracted; [60DUV/LEC], [83BUS/SIB]. [60DUV/LEC] have studied the vibrational frequencies of $I_2O_5(cr)$, including the IOI bridging frequencies. Buss *et al.* [83BUS/SIB], in their discussion of the triatomic molecules XOX , mentioned that the ground state is a singlet. However, there is no additional information as to the precise structure or vibrational frequencies. There are two additional articles; a patent [84DRA/TRI] and a dissertation [31CHI]. The species has not been isolated as a pure compound. No structure is associated with this CAS Registry Number.

5.9 I_2O_2

There is no information to confirm the existence of this compound, which has been reported in the literature four times; in a 1930 review [30BRA], in 1970 [70AMI/TRE], in 1985 [85BUX/SEL], and in 1992 [92MAG/LAV]; in two cases it is suggested as an intermediate compound in an aqueous reaction scheme; whereas in the latter two cases it is presented as an intermediate in the gas phase self-reaction of IO. [70AMI/TRE] suggested dimerization of IO to describe the decay of IO. Similarly, Cox and Coker [83COX/COK], in studying the rate of IO decay, proposed that the initial stages of the reaction involved the formation of I_2O_2 .

5.10 I_2O_3

There is no thermodynamic or spectroscopic information reported for this compound. In fact, this compound has not been isolated or characterized as a separate entity. Although citations are given for this oxide, the discussions only deal with adducts with SO_3 or the like. The CAS Registry Number corresponds to composition I_2O_3 but no structure is associated with this formula.

The references include: [1896CHR], [1898CHR], [12KAP], [35BAH/PAR], [36FIC/DIN], [37MAS], [38MAS], [38MAS/ARG], [54WOO], [57SEM], [57SYM], [59LEH/HES], [60DAS/WAD], [62FIA/TAR], [63PAC/HAU], [64DAE/KJE], [68SEL/KJE], [71SEL/KJE], and [89SAG].

5.11 I_2O_4

The CAS Registry Number corresponding to I_2O_4 has been discontinued. This compound is now referred to as IO_2 . The I_2O_4 unit is normally used in reference to the condensed phase, whereas in solution or gas phases, IO_2 is the entity discussed. For this reason, the literature is somewhat confusing for this compound, since in the early studies, the dioxide was mentioned where, in fact, the I_2O_4 species was really being discussed. There is no thermodynamic information reported for this oxide, although there is some data for the thermal stability (refer to Tables 1a and 1b). There are numerous studies which report structural and vibrational frequency information for the crystalline phase (refer to Table 5).

A CAS Registry Number 99690-81-0 corresponds to iodosyl iodate with the inferred structure $IO^+IO_3^-$. There is one reference to this compound [60DAS/WAD]. Dassent and Waddington [60DAS/WAD, 63DAS/WAD] have provided tentative information concerning the crystalline structure on the basis of infrared spectra, whereas [68SEL/KJE] used a combination of x-ray diffraction, density, ir spectra, proton magnetic resonance, DTA and TGA to examine the formation and stability of $I_2O_4(cr)$. [60DAS/WAD] prepared iodine dioxide by Muir's method [09MUI] and gave frequency assignments for iodine dioxide in terms of I_2O_4 . They state that the formation of I_2O_4 as iodosyl iodate was satisfactory if it was remembered that IO was not present as a discrete cation.

The numerous citations on I_2O_4 may be arbitrarily classified as follows:

1. Preparation/formation
[1884MIL], [1898CHR], [09MUI], [12KAP], [15FIC/KAP], [35BAH/PAR], [39BAH/SIN], [60DAS/WAD], [80WIK/TAY]
2. Reaction
[57SEM], [59LEH/HES], [61VLA/ATI], [62FIA/TAR], [64GIL/SEN], [70KUZ/KOT]
3. Properties
[50WIL/DHA], [57SYM], [62ARO/MIS], [68SEL/KJE]
4. Spectroscopy/structure

- [50WIL/DHA], [60DAS/WAD], [61WIS/HAN],
 [63ALO], [63DAS/WAD], [68GRU/MUR],
 [69GRU/LUR], [71GRU/LUR], [75JON],
 [76DAL/CAR], [81ELL/WOL], [87LEH/CHR]
5. Decomposition
 [35BAH/PAR], [39BAH/SIN], [68SEL/KJE],
 [80WIK/TAY]
6. Review
 [60GEO], [63SCH/BRA], [64DAE/KJE], [71SEL/KJE]

In the presumed confirmation of an earlier study by Wilmarth and Dharmitti [50WIL/DHA], Wise and Hannan [61WIS/HAN] determined the structure of I_2O_4 as $IO^+IO_3^-$. Whereas the former study used magnetic susceptibility measurements, the latter relied on the ir spectra in KBr pellets. Two strong absorption bands were assigned to IO^+ and IO_3^- , with the latter assignment made by comparison with compounds such as alkali metal iodates, MIO_3 .

Lehmann *et al.* [87LEH/CHR] used high resolution synchrotron powder x-ray data and neutron data to solve the structure of I_2O_4 . They determined the dimensions of the unit cell and confirmed the space group was ($P2_1/c$). Prior to this study, the structure was unknown, and only the probable group ($P2_1/c$) and the corresponding unit cell were known from an indexed Guinier diagram.

Grushko *et al.* [68GRU/MUR, 69GRU/LUR], using Mössbauer techniques, proposed a structure with two non-equivalent iodine atoms in which the oxide has a polymeric structure composed of IO_3 and IO groups covalently bonded by oxygen bridges. This study confirms the ir evidence given by [60DAS/WAD, 63DAS/WAD].

5.12 I_2O_5

There are numerous studies on the pentoxide. However, the only direct thermodynamically related information is early references to formation data. (See Table 1.) There are no heat capacity or enthalpy data, or melting information. There are numerous references to the fact that this oxide sublimes.

The discontinued CAS Registry Number 7790-35-4 probably referred to I_2O_5 before its structure was known. The current CAS Registry Number 12029-98-0 refers to I_2O_5 with a structure $O_2I-O-IO_2$.

The numerous citations on I_2O_5 may be arbitrarily classified as follows. Note that the distinction between the categories of reaction, detection, and commercial applications is often not clear.

1. Enthalpy of formation
 [1870DIT], [1878BER], [1882THO], [12GUI],
 [32MOL/PER], [48FAR/KLE], [52ROS/WAG],
 [60SPE/HEP]
2. Preparation/formation
 [1896CHR], [09BEG], [09GUI2], [09GUI3], [09MUI],
 [12GUI], [20LAM/BRA], [31BAX/BUT],
 [31MOL/PER], [32MOL/VIT], [35BAH/PAR],
 [38EMS], [38EMS2], [38MAS], [38MAS/ARG],
 [39EMS], [39EMS2], [39VAH/SIN], [40KOM],
 [53PFL], [55KIK], [58ODE], [58VIL/DRO], [59HAU],
 [61DUP/LEC], [61PAV/RAF], [62FIA/TAR],
 [63PAC/HAU], [64DAE/KJE], [66WAL/PHI],
 [68BAC], [68TOR/KAW], [85VIK/MAC],
 [95AHM/FJE]
3. Reaction
 [1898CHR], [11REI/SCH], [34BAX/HAL],
 [35AST/VAP], [47BAU/BRU], [50EME/WOO],
 [52BAT/SIS], [52YAM/ASA], [58YEE],
 [59LEH/HES], [62FIA/TAR], [62OPA/KUZ],
 [62OPA/KUZ2], [62ORO/MIS], [62SOR/HAR],
 [63EHR/ENG], [64KAI/SCH], [64KAI/SCH2],
 [65KEM/ROB], [66KIR/MUR], [67MUK/END],
 [70AMB/SAI], [70SAI/AMB], [72RAD/DEV],
 [74KAW/SAK], [76PET/VOL], [76RON],
 [77CAM/CHA], [77GIL/SPE], [79DRA/URB],
 [79TOR/SMI], [80GEB/MCN], [80IVA/IVA],
 [80IVA/IVA2], [80IVA/IVA3], [81CHI/SAI],
 [81IVA/IVA], [81SID/NAS], [81VIK/FUR],
 [83DRA/HAV], [84COH], [84COH/MCN],
 [84GOR/AND], [84VIK], [85CAB/BAR],
 [85DRA/HAV], [85MAN/GEO], [87YOS/GOT],
 [88MAL/GUP], [89CHR/WIL], [89MAN/GEO],
 [91LEE/CHA], [94AHM/FJE], [94NUS/WEL],
 [94REE/BRA]
4. Detection
 [29PIR], [31SAH/OZA], [53ADA/SIM], [59ZLO/ZIE],
 [64KAI/SCH3], [66ZIE], [72IMA/OOS],
 [73MAN/BOZ], [76ADA/KAS], [78AGR/KLI],
 [79POD/DEM], [81FED/KOL], [84DRA/HAV],
 [84NAG/SUZ], [85UEH/NAK], [86XU/WU],
 [89HON/HAR], [90SHE/ZAH], [91LE],
 [94SAT/YAM]
5. Decomposition
 [07BER], [08GUI], [09GUI], [11GUI], [31MOL/PER],
 [32MOL/PER], [32MOL/VIT], [57DUV], [57DUV2],
 [67STU/HUS], [70SHE/TUR2], [75JAK/SOL],
 [80WIK/TAY], [85VIK/MAC]
6. Commercial applications
 [22KAT/BLO], [39OZH], [44SCH], [48EMB],
 [54NAI/SIG], [54NAI/SUG2], [55WAC], [56PAC],
 [58HAL/JAM], [58IMA], [63SEN/KOP], [65KNA],
 [67MAR/IDE], [77COL/NAG], [79KAN/YOS],
 [79KOT/TAK], [80HOF/SPI], [81GLU/GRI], [81HOF],
 [81HOF/SPI], [86MIS/PAT]
7. Properties

[23LAM/PHI], [30GRA/FAR], [32HUL/BLI],
 [32MOL/PER], [36MOL/DIL], [36VIL/MOL],
 [38WEB], [40BAK/KEL], [54SHI/KOS],
 [55KOJ/TSU], [60DUV/LEC], [62ARO/MIS],
 [66SOB/VAN], [68SEL/KJE], [68VEP/HAU],
 [70SEL/KJE], [70SHE/TUR], [73SEM/MOS],
 [75BAR/BUL], [76DAL/CAR], [76SHE],
 [77OKU/GOT], [78CHR/WIL], [78CER/KO],
 [78PET/BOG], [79PET/VOL], [80RUB/SAS],
 [81ELL/WOL], [84GOR/AND], [85SUN/WRE]

8. Hydrate

[33GAR], [33MOL/PAR]

9. Review

[51ADA/SIM], [54COU], [60GEO], [63SCH/BRA],
 [71SEL/KJE], [76LEL]

10. Ternary systems

[51RIC/AMR], [52RIC/FRE], [56NIK/BUS]

There has been extensive work on the preparation, crystal structure, Raman spectra, and decomposition. The crystal structure studies suggest that the molecule is of the form $\text{IO}_2\text{-O-IO}_2$. TGA and DTA results consistently show that I_2O_5 decomposes in the range 570–730 K to the elements [68SEL/KJE, 85VIK/MAC].

Farkas and Klein [48FAR/KLE] reported an enthalpy of formation for $\text{I}_2\text{O}_5(\text{cr})$ as -42.0 kcal/mol, but do not give any source for this number. The enthalpy of formation value (-37.78 kcal mol $^{-1}$) recommended by Brewer and Rosenblatt is the value recommended by Wagman *et al.* (1968). The value recommended by Glushko and Medvedev is -43.8 kcal mol $^{-1}$.

The 1982 republication of Wagman *et al.* recommended an enthalpy of formation for I_2O_5 based on a study by Spencer and Hepler (1960). The evaluation was performed in 1964. The study involved the reaction of $\text{I}_2\text{O}_5(\text{cr})$ with aqueous KOH. There are no recent calorimetric determinations of $\Delta_f H^\circ$ either through formation from or decomposition to the elements. At the time of the Wagman evaluation, four other solution processes led to formation values within 1.3 kcal mol $^{-1}$ range.

5.13 I_2O_6

The study of I_2O_6 is confusing since we must examine four different species: (1) iodyl periodate [77SEI/WEI], (2) iododioxigen periodate [77SIE/WEI], (3) iodine oxide, and (4) iodine trioxide (IO_3). Early references were to IO_3 and an unspecified I_2O_6 . It is not clear as to which species truly exists in the condensed phase.

The references for the discontinued CAS Registry Number for I_2O_6 (64052-04-6) are not included under IO_3 references. Via a Chemical Abstract literature search, there is one I_2O_6 reference [77SIE/WEI] referring to iododioxigen periodate with a presumed structure $\text{IO}_2^-\text{IO}_4^-$. However, [77SIE/WEI] referred to I_2O_6 in its study as iodyl periodate which was

given a Registry Number of 63912-61-8 in CAS. No references are listed under this registry number.

The early references for IO_3 in fact discussed I_2O_6 . This compound was presumably formed by the decomposition of periodic acid [1861KAE], [58ODE], [63PAC/HAU] and orthoperiodic acid, H_5IO_6 [59HAU]. Only one paper presents evidence in which this species was isolated; Siebert *et al.* [77SIE/WEI] confirmed its existence. The compound was prepared by two techniques and was confirmed as a distinct species by its individual Raman spectra. Diamagnetism studies proved that it is a mixed valence entity; perceived as iodyl periodate, $\text{IO}_2^+\text{IO}_4^-$, as discussed in Table 5. There are no thermodynamically related data.

A recent study [95KRA/JAN] determined the crystal structure of I_2O_6 as a mixed valent oxide, I(V/VII).

Alternatively, Wagner and Strehlow [82WAG/STR] suggest that this species supposedly formed from the dimerization of the IO_3 radical in aqueous periodate solutions as a result of flash photolysis.

5.14 I_2O_7

This condensed phase compound has not been isolated or characterized. It is often cited in terms of being the end member in ternary systems, but the I_2O_7 portion of the triangular diagram has not been studied. There are fourteen references for this compound: six preparations and eight ternary systems ($\text{X-I}_2\text{O}_7\text{-H}_2\text{O}$). I_2O_7 is considered the hypothetical anhydride of periodic acid H_5IO_6 .

The current CA Registry Number refers to an iodine-oxygen compound in which the atomic ratio is 2:7 but no structure is given. (There is a discontinued CA Registry Number 20270-38-6.)

The ternary systems are as follows:

[51GYA] $\text{Ag}_2\text{O-I}_2\text{O}_7\text{-H}_2\text{O}$
 [53HES/SOU] $\text{I}_2\text{O}_7\text{-Li}_2\text{O-H}_2\text{O}$
 [64DRA/TER] $\text{I}_2\text{O}_7\text{-CaO-H}_2\text{O}$ and $\text{BaO-I}_2\text{O}_7\text{-H}_2\text{O}$
 [66DRA/KOS] $\text{I}_2\text{O}_7\text{-MgO-H}_2\text{O}$
 [68PAC/BOH] $\text{I}_2\text{O}_7\text{-Cd}_3(\text{IO}_3)_2\text{-H}_2\text{O}$
 [74ODE/HEJ] $\text{I}_2\text{O}_7\text{-N}_2\text{O}_5\text{-H}_2\text{O}$ and $\text{I}_2\text{O}_7\text{-SO}_3\text{-H}_2\text{O}$
 [67BIA/SAB] $\text{I}_2\text{O}_7\text{-K}_2\text{O-H}_2\text{O}$
 [67SAB/BIA] $\text{I}_2\text{O}_7\text{-Na}_2\text{O-H}_2\text{O}$.

The following citations deal with the preparation and subsequent decomposition of I_2O_7 :

- [58ODE] studied the dehydration of H_5IO_6 ;
- [62MIS/SYM] dealt with the formation from the reaction of H_5IO_6 with concentrated sulfuric acid (deduced that the compound was unstable; isolation often resulted in decomposition with explosive violence);
- [63PAC/HAU] dealt with the thermal decomposition of H_5IO_6 and the possible formation of a product of the form $\text{I}_2\text{O}_7 \cdot \text{I}_2\text{O}_5$; [68SEL/KJE], whose data was consistent with the results of [63PAC/HAU].
- Wagner and Strehlow [82WAG/STR] suggested a reaction scheme in which ozone oxidized I_2O_6 to I_2O_7 .

Chladek and Troenel [93CHL/TRO] established a relationship between the bond length and the bond strength for numerous oxides.

5.15 I₂O₈

This condensed phase compound has not been isolated or characterized. It is postulated to exist in aqueous reaction schemes. The CAS Registry Number corresponds to the structure O₃I-OO-IO₃.

Wagner and Strehlow [82WAG/STR], in the flash photolysis of periodate in the pH range 2.44 to 4.90 using conductometric detection, observed three reactions, one of which was attributed to the hydrolysis of I₂O₈. The authors stated that ozone oxidized IO₃ to form IO₄, which in turn dimerized to I₂O₈. This citation provided no indication of the structure.

5.16 I₄O₉

There are sufficient reliable studies to indicate that this compound does exist in the crystalline phase. The current CAS Registry Number corresponds to a structure I(IO₃)₃ and a name, iodine iodate. (A discontinued CAS Registry Number 73560-00-6 also exists, which most likely refers to an I₄O₉ species with an unknown structure.) There are no studies which provide numeric thermodynamic information. That is, there are no studies on the heat capacity, enthalpy, melting, or enthalpy of formation.

The information on I₄O₉ may be arbitrarily classified as follows:

1. Preparation/formation
[09BER], [09FIC/ROH], [15FIC/KAP], [35BAH/PAR], [55KIK], [68SEL/KJE], [80WIK/TAY], [83COX/COK], [85SUN/WRE], [85VIK/MAC]
2. Decomposition
[35BAH/PAR], [55KIK], [80WIK/TAY]
3. Reactions/intermediates
[61VLA/ATI], [62ARO/MIS], [80WIK/TAY]
4. Review
[63SCH/BRA]
5. Iodine transport
[81VIK/FUR], [84VIK], [89SAG]
6. Characterization (crystal)
[85SUN/WRE]

There are many articles which deal with the formation of I₄O₉ and the subsequent decomposition to I₂O₅. There are

three preferred methods of preparation: (1) the reaction of I₂ with ozone, (2) thermal treatment of iodine with anhydrous HPO₃, and (3) heating iodic acid with orthophosphoric acid. This oxide decomposes above 350 K to yield the pentoxide (I₂O₅). See Table 1b for details. Additional studies include irradiation [61VLA/ATE], a magnetic susceptibility measurement [62ARO/MIS], and Raman spectra [85SUN/WRE].

The experimental studies by Selte and Kjekshus [68SEL/KJE] did not support the results of [15FIC/KAP] and [35BAH/PAR]. By following the procedures of the latter two studies, Selte and Kjekshus could not produce I₄O₉. In addition these results also suggested that the reactions between iodine and ozone took place in CCl₄ solutions rather than in the gas phase, in contrast to [09BER] and [55KIK]. Selte and Kjekshus did not comment on the formation of I₄O₉ as described in [09FIC/ROH].

Sunder *et al.* [85SUN/WRE] isolated amorphous and crystalline I₄O₉ and determined the Raman spectra. They established conclusively that it was a distinct molecular species and not a mixture of I₂O₅ and I₂O₄. This study provided tentative vibrational assignments for five types of vibrations (I=O stretch, O-I=O symmetric stretch, I-O stretch, OIO deformation, IOI deformation). The vibrational frequency assignments were made by analogy with I₂O₄ and I₂O₅.

5.17 I₆O₁₃

The earliest reference dealing with the preparation of this solid compound is by Kaemmerer (1861).

The study by Kappeler [12KAP] questioned the existence of this oxide and indicated that it was most probably I₂O₄. This conclusion was further supported by [64DAE/KJE]. There are no studies since 1912 which have been able to prepare this species. This compound is assumed not to exist.

5.18 I₁₀O₁₉

The earliest reference dealing with the preparation of this solid compound is by Millon (1844/45).

The study by Kappeler [12KAP] questioned the existence of this oxide and indicated that it was most probably I₂O₄. This conclusion was further supported by [64DAE/KJE]. There are no studies since 1912 which have been able to prepare this species. This compound is assumed not to exist.

TABLE 1a. Solid iodine oxide species: Preparation and related reactions

Source	Reaction	Temperature	Comments
IO			
81GRO/LAU	Quadrupole coupling constants for ^{127}I		Comparison of calculated and experimental values; reference to earlier experimental study?
IO₂ (I₂O₄)			
86BYB	Formation of IO ₂ from the photolysis and x -irradiation of IO ₄ ⁻ embedded in KClO ₄	26 K	Observation and calculation of ESR spectra to determine structure
1844MIL	I ₂ + HNO ₃ → I ₂ O ₄ H ₂ SO ₄ + HIO ₃ → I ₂ O ₄		
15FIC/KAP	Preparation of IO · IO ₃		Reference to earlier preparative procedures by 1844 Millon
35BAH/PAR	H ₂ SO ₄ (hot, conc.) + HIO ₃ → I ₂ O ₄	[85 °C]	Reaction gives yellow granular nonhygroscopic I ₂ O ₄ which, when heated above 85 °C forms I ₂ O ₅
62FIA/TAR	I ₂ O ₃ + I ₂ O ₅ - 2(IO)(IO ₃)	138-210 °C	I ₂ O ₃ , formed by I ₂ -I ₂ O ₅ radioactive exchange system reacts with excess I ₂ O ₅ to yield I ₂ O ₄
64GIL/SEN	HIO ₃ + H ₂ SO ₄ → (IO) _n		Cryoscopy used to determine T_{fus} (for information, see Table 1, pp. 973-4) of I ₂ O ₄ in sulfuric acid solutions; interpolation; used method of 35BAH/PAR
IO₃			
48FAR/KLE	Formation of IO ₃		$\Delta_f H^\circ = -28 \text{ kcal mol}^{-1}$ is stated as calculated for IO ₃ , but the formula given is IO ₃ ⁻
I₂O			
38MAS	IO ₂ important as intermediate in the reverse reaction involving 3.5H ₂ SO ₄ , H ₂ O and I ₂ O ₃ · SO ₃ (c)		Reversibility exists for IO ₂ due to lack of high concentration of acid
I₂O₂			
85BUX/SEL	IO + IO → I ₂ O ₂ I ₂ O ₂ + H ₂ O - HOI + IO ₂ ⁻ + H ⁺		Proposed reaction scheme leading to formation of iodate ion in solution
I₂O₃			
35BAH/PAR	Preparation apparently involves I ₂ O ₃ and H ₂ SO ₄ complex		Preparation of I ₂ O ₃ and I ₂ O ₃ in sulfate compounds: I ₂ O ₄ , H ₂ SO ₄ and I ₂ O ₃ , H ₂ SO ₄ , respectively
38MAS	2I ₂ + 3I ₂ O ₅ = 5I ₂ O ₃ : shaken yellow solution + I ₂ O ₃ · SO ₃ (c)		In concentrated sulfuric acid, I ₂ O ₃ · SO ₃ takes up elementary iodine to form a brown solute; I ₂ O ₃ was not isolated, only the complex with sulfuric acid
62FIA/TAR	I ₂ + I ₂ O ₅ - [I ₂ O ₃] - I ₂ + I ₂ O ₅	138-210 °C	The exchange of iodine in the I ₂ -I ₂ O ₅ systems has been studied by use of radioactive isotope ^{131}I
I₂O₅			
12GUI2	Examined the exothermic reaction: I ₂ (g) + O ₂ (g) → I ₂ O ₅ (c)	173 °C	Equilibrium pressure of system was calculated to 173° based on the earlier Berthelot data; concluded that direct oxidation of iodine is not a create practical preparation of anhydride; refers to two earlier studies of Berthelot and Thomsen in which enthalpy of formation is given
31BAX/BUT	Formation from dehydration of HIO ₃		I ₂ O ₅ produced by dehydration of HIO ₃ contains less I (and more O) than corresponds to the theoretical formula
35BAH/PAR	H ₂ SO ₄ (hot, conc.) + HIO ₃ → I ₂ O ₄ ozonized O ₂ + I ₂ (g) → I ₄ O ₉	[85 °C]	Action of HNO ₃ on I ₂ gives hygroscopic I ₂ O ₅ ; I ₄ O ₉ reaction occurs in vapor phase; yellow hygroscopic crystals obtained; decomposition between 85 and 120° gives I ₂ O ₅
36VIL/MOL	Formation of 3I ₂ O ₅ · H ₂ O from reaction of hot I ₂ with HNO ₃		Formation of I ₂ O ₅ by dehydration of hydrate <i>in vacuo</i> over KOH
38MAS	2I ₂ + 3I ₂ O ₅ = 5I ₂ O ₃ : shaken yellow solution + I ₂ O ₃ · SO ₃ (c)		In concentrated sulfuric acid, I ₂ O ₃ · SO ₃ takes up elementary iodine to form a brown solute
40KOM	Formation by heating HIO ₃		Directions for production of HIO ₃ and subsequent preparation of I ₂ O ₅
48FAR/KLE	No experimental procedure for formation of I ₂ O ₅		$\Delta_f H^\circ = -42.0 \text{ kcal mol}^{-1}$ enthalpy of formation is stated; no reference given to the source of this value
57DUV	Step-wise dissociation: sublimation of HIO ₃ -I ₂ O ₅	248-410 °C	Infrared absorption spectra observed and compared with earlier studies; rapid dissociation and sublimation above 410 °C; no enthalpy values given

TABLE 1a. (Continued.)

Source	Reaction	Temperature	Comments
57DUV2	Preparation of mixture: $2\text{KIO}_3 + \text{I}_2\text{O}_5$	180–370 °C [500 °C]	Infrared absorption spectra studies; iodic anhydride disappears at 500 °C with the start of dissociation and sublimation
62FIA/TAR	Reversible redox reaction: $\text{I}_2 + \text{I}_2\text{O}_5 \rightleftharpoons [\text{I}_2\text{O}_3] + \text{I}_2 + \text{I}_2\text{O}_5$ energy of activation = 10 kcal mol ⁻¹	138–210 °C	The exchange of iodine in the I ₂ –I ₂ O ₅ systems has been studied by use of radioactive isotope ¹³¹ I
84VIK	Preparation		Uses uv light; I ₂ then reacted with O ₃ to form solid I ₄ O ₉ or I ₂ O ₅
I₂O₇ 62MIS/SYM	$\text{H}_5\text{IO}_6 + 65\% \text{ oleum} \rightarrow \text{I}_2\text{O}_7$		Spectrophotometry; assumed of new solid formation to be I ₂ O ₇ <i>in vacuo</i>
I₄O₉ 15FIC/KAP	Formation of I(IO ₃) ₃		Two references to earlier preparation procedures: 1909 Fichter and Rohner; 1906 Beger
35BAH/PAR	Ozonized O ₂ + I ₂ (g) → I ₄ O ₉		Reaction occurs in vapor phase; yellow hygroscopic crystals obtained; decomposes at 75 °C
55KIK	$\text{O}_3 + \text{I}_2(\text{g}) \rightarrow \text{I}(\text{IO}_3)_3$	45–50 °C	Ozone reaction with iodine vapor to form I ₄ O ₉ containing some unoxidized iodine
84VIK	Preparation		Uses uv light; I ₂ then reacted with O ₃ to form solid I ₄ O ₉ or I ₂ O ₅
85VIK/MAC	Formation: $4\text{I}_2(\text{g}) + 6\text{O}_3 \rightarrow 2\text{I}_4\text{O}_9(\text{c})$	293–370 K	Stoichiometric composition of I ₄ O ₉ in flow system; kinetic data given
I₆O₁₃/I₁₀O₁₉ 12KAP	Preparation		Using earlier preparation method, the author suggests that the two oxides were misidentified and should be IO · IO ₃

TABLE 1b. Solid iodine oxide species: Decomposition and related reactions

Source	Reaction	Temperature	Comments
IO 67STU/HUS	Decomposition		Mass spectra; no values given; IO ⁺ and IO ₂ ⁺ undergo marked fluctuations in intensity; independent existence for IO ₂ in gases produced by vaporization of I ₂ O ₅
IO₂(I₂O₄) 09MUI IO ₂ /I ₂ O ₄	Decomposition: I ₂ + O ₂	130 °C	Aqueous compositions/mixtures mostly; molecular weight not determined (IO ₂ or I ₂ O ₄); density values given; I ₂ O ₄ is not hygroscopic
35BAH/PAR	Decomposition: $5\text{I}_2\text{O}_4 = 4\text{I}_2\text{O}_5 + \text{I}_2$	*110, 125, 130 °C	*I ₂ O ₄ decomposes slowly at 85 °C but more rapidly at 130 °C; decomposition does not proceed as stated by 09MUI; it is not hygroscopic
64DAE/KJE	Decomposition: $5\text{I}_2\text{O}_4 - 4\text{I}_2\text{O}_5 + \text{I}_2$ $5\text{I}_2\text{O}_4 + 4\text{H}_2\text{O} - \text{I}_2 + 8\text{HIO}_3$	100–230 °C 20–240 °C	Decomposition in moist air; thermogravimetric analysis; x-ray diffraction investigation; density values given
68SEL/KJE	Decomposition: $5\text{I}_2\text{O}_4 = 4\text{I}_2\text{O}_5 + \text{I}_2$	125–250 °C	Differential thermogravimetric (DTG) analysis data (215–260 °C; 300–415 °C); x-ray diffraction data; proton magnetic resonance studies; density measurements included
71SEL/KJE	Decomposition: $3\text{I}_2\text{O}_4 - 4\text{I}_2\text{O}_5 + \text{I}_2$	125–250 °C	Statement of previous observations
80WIK/TAY	Decomposition: $9\text{I}_2\text{O}_4 - 4\text{I}_4\text{O}_9 + \text{I}_2$ $5\text{I}_2\text{O}_4 - 4\text{I}_2\text{O}_5 + \text{I}_2$	460 K	Thermogravimetry; x-ray diffraction measurements; differential thermal analysis (DTA)
I₂O₃ 62FIA/TAR 63PAC/HAU	$\text{I}_2\text{O}_3 + \text{I}_2\text{O}_5 = 2(\text{IO})\text{IO}_3$ Decomposition of orthoperiodic acid (H ₅ IO ₆) – I ₂ O ₅ ; I ₂ O ₇	138–210 °C 105–117 °C	Reaction with excess I ₂ O ₅ Thermogravimetry; possible classification of product as IO ₃
I₂O₅ 1898CHR2	Decomposition/reaction with H ₂ O: 3(SO ₃ · 3H ₂ O) + I ₂ O ₅ · H ₂ O · SO ₃ · H ₂ O · I ₂ O ₄ + 1/2 I ₂ O ₅ · 4I ₂ O ₅ + I ₂ O ₄ + SO ₃ · H ₂ O: 2I ₂ O ₅ + I ₂ O ₄ – SO ₃ · H ₂ O	1. Decomposition 200 °C	Decomposition in contact with humid air, water, or alcohol; preparation of crystallized substance

TABLE 1b. (Continued.)

Source	Reaction	Temperature	Comments
31MOL/PER	Decomposition	275 °C	Decomposition of pure dry I ₂ O ₅ in dry air
32MOL/VIT	Decomposition ?ΔH° dissociation = -9.2 kcal mol ⁻¹ ΔH° hydration = 2.1 kcal mol ⁻¹	275 °C	Initial temperature of decomposition; ΔH° reactions are deduced
32MOL/VIT2	Initial decomposition: I ₂ O ₅ - I ₂ + O ₂	275 °C	Decomposition of I ₂ O ₅ at 275 °C is determined by the modified method of Tzentnershver and Andrusov; ΔH solution of I ₂ O ₅ given presumably in water
38MAS/ARG	Decomposition: I ₂ O ₅ - I ₂ O ₃ + O ₂	215-220 K	Chretien's iodosulfate; reaction occurring in fuming sulfuric acid; product stabilized as an iodosulfate
64DAE/KJE	Decomposition: I ₂ O ₅ - O ₂ + I ₂	330-460 °C	Decomposition; thermogravimetric analysis; x-ray diffraction investigation
67STU/HUS	Decomposition		Mass spectra; no numeric information provided; six ions detected; HIO ₃ dehydrated to I ₂ O ₅ ; sufficient volatilization occurred so that mass spectrum could be obtained
68SEL/KJE	Decomposition: 2I ₂ O ₅ = 2I ₂ + 5O ₂ sublimation	>[280 °C] [250 °C]	Differential thermogravimetric analysis data (355-420 °C); x-ray diffraction data; crystallization from aqueous solutions with degrees of acidity; density measurements included
78CER/KO	Reaction: $\frac{1}{2}I_2O_5(c) + \frac{1}{2}H_2O(l)$ = H ⁺ (aq) + IO ₃ ⁻ (aq) $\frac{1}{2}I_2O_5(c) + OH^-(aq)$ = IO ₃ ⁻ (aq) + $\frac{1}{2}H_2O(l)$	25 °C	Proton magnetic resonance studies; ir studies Calorimetric measurements of enthalpies of both reactions; prime rotational was to determine the enthalpy of ionization of water; enthalpy of reaction = 13.34 kcal mol ⁻¹
80WIK/TAY	Decomposition: 2I ₂ O ₅ - 2I ₂ + 5O ₂	[600]-710 K	Thermogravimetry; x-ray diffraction measurements; differential thermal analysis
85VIK/MAN	Decomposition: 2I ₂ O ₅ (c) - 2I ₂ (g) + 5O ₂ (g)	570-730 K	TGA and DTA study of I ₂ O ₅
I ₂ O ₅	2. Decomposition Reactions Leading to I₂O₅		
09GUI	Decomposition: I ₂ O ₅ - I ₂ + O ₂	350-270 K	Reaction of iodine anhydride when exposed to heat; reaction starts at 350 K but gradually reaches 270 K by the end; preparation of substances
09MUI	I ₂ O ₅ + SO ₃	100 °C	Similar to earlier studies by Kammerer and Weber; presumed product is I ₂ O ₅ ·2SO ₃ which differs from results of other two studies
11GUI	Decomposition of anhydride	250 °C	Preparative technique of anhydride; study of decomposition in vacuum
12GUI	Decomposition of I ₂ O ₅ into iodic acid and oxygen	250 °C	Decomposition in vacuum, during 100 hours
32MOL/VIT2	Stepwise dehydration: HIO ₃ - I ₂ O ₅ ·H ₂ O - I ₂ O ₅	70 °C	The systematic thermal dehydration of HIO ₃ yielded 3I ₂ O ₅ ·H ₂ O at 70 °C; at higher temperature, loss of H ₂ O is very small up to 200 °C where total dehydration gives I ₂ O ₅
59HAU	Stepwise decomposition: H ₅ IO ₆ - I ₂ O ₅	115-151 °C	Thermal decomposition
61PAV/RAF	Decomposition of NH ₄ IO ₃ in vacuum to form I ₂ O ₅	100-170 °C	Decomposition of NH ₄ IO ₃ studied manometrically to form I ₂ O ₅ , but it did not involve HIO ₃ as an intermediate; I ₂ (g) was also a product
68SEL/KJE	Decomposition of 2HI ₃ O ₈ 3I ₂ O ₅ + H ₂ O	190-250 °C	Discussion on I ₂ O ₅ sublimation; DTG data (355-420 °C); x-ray diffraction data; recrystallization from aqueous solutions with degrees of acidity; density measurements included
71SEL/KJE	Decomposition: 3I ₂ O ₄ - 4I ₂ O ₅ + I ₂	125-250 °C	Statement of previous observations

TABLE 1b. (Continued.)

Source	Reaction	Temperature	Comments
I₄O₉			
35BAH/PAR	Decomposition: $4\text{I}_4\text{O}_9 \rightarrow 6\text{I}_2\text{O}_5 + 2\text{I}_2 + 3\text{O}_2$	*85–120 °C	*I ₄ O ₉ begins to decompose at 75 °C but reaches its peak at 85–120 °C; it is very hygroscopic; comments on many reactions of I ₄ O ₉ are also given
80WIK/TAY	Decomposition: $5\text{I}_4\text{O}_9 \rightarrow 9\text{I}_2\text{O}_5 + \text{I}_2$	415–460 K	Thermogravimetry; x-ray diffraction measurements, differential thermal analysis
83COX/COK	Decomposition: $5\text{I}_4\text{O}_9 \rightarrow 9\text{I}_2\text{O}_5 + \text{I}_2$	460 K	Authors state that these data from [80WIK/TAY] are consistent with observations in their system
85SUN/WRE	Decomposition: $5\text{I}_4\text{O}_9 \rightarrow 9\text{I}_2\text{O}_5 + \text{I}_2$		Crystalline compound thermal decomposition—see 85VIK/MAK
85VIK/MAK	$\text{I}_4\text{O}_9 \rightarrow \text{I}_2\text{O}_5 + \text{I}_2$		Thermogravimetry and differential thermal analysis of I ₄ O ₉ indicates two transitions, the last one of which appears to be the decomposition of I ₂ O ₅

TABLE 2. Iodine oxide species: Neutrals, radicals, and ions in solution

Source	Compound	Reaction	Temperature	Comments
1896CHR	I ₂ O ₃ I ₂ O ₅	Decomposition: 3I ₂ O ₃ + H ₂ O = 2I ₂ O ₅ + H ₂ I ₂ 5I ₂ O ₃ = 3I ₂ O ₅ + 2I ₂	250–260 °C	Immediate decomposition in contact with H ₂ O; HI cannot exist in the presence of iodic acid, hence the second reaction
1898CHR2	I ₂ O ₃ I ₂ O ₅	Decomposition: 3I ₂ O ₃ + H ₂ O = 2I ₂ O ₅ + H ₂ I ₂ 5I ₂ O ₃ = 3I ₂ O ₅ + 2I ₂	250–260 °C	Immediate decomposition in contact with water; HI cannot exist in presence of iodic acid, hence the second reaction
23GOM	IO ₄	(ClO ₄) + I = (IO ₄) + Cl; equilibrium		Probable formation of IO ₄ in ether; IO ₄ presumably unstable to I ₂ and O ₂
30BRA	I ₃ O ₂ I ₂ O ₂	I ₃ O ₂ ⁻ - I ₂ O ₂ - H ₂ I ₂ O ₃ I ₂ O ₂ + H ₂ O - H ₂ I ₂ O ₃ ;	25 °C	I ₂ O ₂ proposed as an intermediate in the reaction between iodate and iodide ions; refers to many previous iodine-oxide ion studies
36FIC/DIN	I ₂ O ₃	*Preparation of I ₂ O ₃ · SO ₃ ^{1/2} H ₂ O		*Preparation of I ₂ O ₃ · SO ₃ ^{1/2} H ₂ O but no data of I ₂ O ₃ itself
48FAK/KLE	IO ₃	Formation of IO ₃ from photodecomposition of iodate ion in solution		It appears that the Δ _r H° calculated value is for the radical not the ion, as indicated in the article
72FOR/GOO	I ₂ O	Hypoiodate reaction: HgO + 2I ₂ - HgI ₂ + I ₂ O I ₂ O - I ₂ + 1/2 O ₂	18 °C	Stability and reactivity of mercuric oxide with iodine reagent in solution; these reactions (among others) are proposed to describe the hypoiodate reaction
74ODE/DEJ	I ₂ O ₇	Solubility of I ₂ O ₇ in ternary systems	0; 25; 50 °C	Solubility in the I ₂ O ₇ -N ₂ O ₅ -H ₂ O and I ₂ O ₇ -SO ₃ -H ₂ O systems studied; I ₂ O ₇ was never isolated
80COO	IO ₂ IOO	Chloride ion; catalyzed oxydation reaction scheme	25 °C	Kinetic data; chloride ions may influence the production of the free radical iodine dioxide; IO ₂ and IOO are intermediates in the reaction scheme; no thermochemical data present
81KLA/SEH	IO ₃ ⁻	IO ₃ ⁻ + O ⁻ - IO ₂ ²⁻ (IO ₃) ₂ IO ₃ ⁻ + OH - IO ₃	21 + 2 °C	Radiolysis and flash photolysis of aqueous iodate and periodate solutions; Δ _r G°(IO ₃) = 190 kJ/mol, presumably in aqueous solution; spectrum and decay kinetics of the assumed IO ₃ are determined
82FUR/NOY	IO IO ₂	Oscillatory Briggs- Rauscher reaction (acidic aqueous solution)	25 °C	Postulates that IO and IO ₂ exist as intermediates in acidic aqueous reactions in the kinetic description of this reaction
82NOS/NOS	I ₂ O	Oscillatory reactions for ion selective electrodes	24 ± 1 °C	Preparation of iodide-free HOI; IO ₂ in an intermediate
83WAG/STR	IO ₄ I ₃ O ₈ IO ₃ I ₃ O ₆	Hydrolysis: I ₂ O ₈ + H ₂ O - IO ₃ ⁻ + IO ₄ ⁻ + 2H + O ₂ I ₃ O ₆ + H ₂ O - IO ₄ ⁻ + IO ₃ ⁻ + 2H Dimerization: 2IO ₃ - I ₂ O ₆ 2IO ₄ - I ₂ O ₈	278–298 K	Flash photolysis of periodate in pH range 2.44–4.90; IO ₃ formed in the photolysis can be further reacted with O ₃ to form IO ₄ ; both IO ₃ and IO ₄ can further dimerize; all species used to describe kinetics
85BUX/SEL	IO I ₂ O ₂	*IO + IO - I ₂ O ₂	25 °C	Pulse radiolysis of iodide and iodate solutions; spectrophotometry of IO; equilibria in periodate solutions; *in analogy with Cl and Br systems authors suggest formation of I ₂ O ₂ ; dimerization of IO to I ₂ O ₂ proposed to explain kinetics in alkaline solution
86VIK/TOR	IO _x	Gas phase reaction to form oxides followed by reaction/solution with H ₂ O		I ₂ (g) reacts with O ₃ to form iodine oxides that, on contact with H ₂ O, would be washed into the aqueous phase as IO ₃

TABLE 3. Iodine oxide species: Electronic energy levels

Source	Transition	Energy level (cm ⁻¹)	Comments
IO(g)			
37VAI		21 557	T_e value; gas phase study
48COL/GAY	B-X system	$\nu_e=21\ 565$	Flame spectra data; estimated vibrational constants for both states; provides comments on earlier studies by Vaidya and by Blake and Iredale
58DUR/RAM	(² $\Pi_{1/2}$, ² $\Pi_{3/2}$)-X	23 420.3, 22 958.9, 22 478.0, 21 981.9, 21 804.5, 21 481.4	Absorption spectra of IO during flash photolysis of I ₂ O ₂ mixtures; vibrational analysis consistent with scheme developed by Coleman, Gaydon, and Vaidya
60DAS/WAD			Spectra for IO ⁺ estimated by analogy with the oxygen molecule; IO ⁺ is paramagnetic; vibrational absorption spectra of about 800 cm ⁻¹ or higher is estimated in analogy to TeO frequency of 796 cm ⁻¹ ; no electronic energy level info. provided for IO
60DUR/LEG	A ² Π -X ² Π	24 390-15 873	Rotational and vibrational analysis for methyl iodide flame bands; emission spectra for A ² Π -X ² Π transition; $B_e(X^2_{3/2})=0.340\ 26\ \text{cm}^{-1}$; $r_e=1.8676\ \text{\AA}$
61PHI/SUG		18 843	Flame photometry; emission spectra; measured intensity of the (0,4) band; dissociation energy derived
65SIN/RAI	² Π -X ² Π	21 565	Using data from 1960 Durey, Legay, and Ramsey, the RKR potential energy curves were calculated for the X ² Π and A ² Π states
70AMI/TRE		22 222.2	Flash photolysis of IO ₃ ⁻ and IO ⁻ in aqueous solution; absorption spectra in decay kinetics studied by pulse radiolysis; maximum intensity of absorption band at 450 nm
70AMI/TRE2		21 739.1	Flash photolysis of IO ₃ ⁻ in boric acid glass; maximum intensity of absorption band at 460 nm
70CLY/CRU	A ² Π -X ² Π	21 277-23 923	Band absorption spectrophotometry
72BRO/BYF			Estimated spin orbit coupling; A=2330 cm ⁻¹
73SAI	² Σ^+ A ² Π -X ² Π	[30 000]	Estimated value of excited state in comparison with ClO radical; energy separation of ² $\Pi_{1/2}$ and ² $\Pi_{3/2}$ is 2330 cm ⁻¹ ; $B_e(^2\Pi_{3/2})=10\ 157.08\pm 0.18\ \text{MHz}$; microwave spectra; $r_e=1.8677\pm 0.0028\ \text{\AA}$ value is calculated from effective rotational constant $B_e(^2\Pi_{2/3})$ combined with α_e from A ² Π -X ² Π transition of 60DUR/LEG; comparison of molecular constants given
77CAL/MET	B ² Π -X ² Π ?	*50 000-55 555.5 [49 615.5; 50 403.2; 48 959.6]	Fluorescence absorption spectra; *flash photolysis of I ₂ O ₂ mixtures leads to formation of IO by light absorption and optical filters; (?) new system with 3 bandheads observed in ultraviolet
83BEK/MEE	A ² $\Pi_{3/2}$ -X ² $\Pi_{3/2}$	22 469.8	High resolution molecular-beam laser excitation spectroscopy; microwave optical double resonance; equilibrium rotational constant $B_e=10\ 083\ \text{MHz}$ derived using estimated $A_{De}=233\ \text{cm}^{-1}$; calculated vibrational frequency ω_e of 669.7 and corresponding equilibrium internuclear distance $r_e=0.187\ 84\ \text{\AA}$; spin-orbit coupling constrained to be A=2330 cm ⁻¹
83COX/COK	A ² Π -X ² Π	21 277-24 096	No direct analysis of the vibrational and rotational structure; absorption by molecular modulation technique
85BUX/SEL		20 408	Radiolysis spectrophotometry of aqueous HOI; spectra of IO obtained by oxidation of IO ⁻ with O ⁻ in aqueous solution at pH \geq 13; band maximum reported
89RED/RAO	0		Potential energy curves for the ground state constructed by Rydberg-Klein-Rees method as modified by Vanderslice <i>et al.</i> ; no values given; dissociation energy provided
IO(matrix)			
80LOE/MIL	A ² Π -X	21 043 \pm 34	Absorption and emission spectra of IO in solid argon matrix at 20 K; T_e values; prepared by microwave discharge

TABLE 3. (Continued.)

Source	Transition	Energy level (cm ⁻¹)	Comments
IO₂(cr) 69BAR/GIL		20 833.3	Absorption spectra; flash photolysis of aqueous solutions of iodate ions; maximum absorption band at 480 nm attributed to IO ₂ radical
70AMI/TRE		[29 411.8]	Flash photolysis of IO ₃ ⁻ and IO ⁻ in aqueous solution; absorption spectra in decay kinetics studied by pulse radiolysis; estimated value, maximum intensity of band structure at approximately 715 nm
70AMI/TRE2		15 267.2	Flash photolysis of IO ₃ ⁻ in boric acid glass; maximum intensity absorption band at 655 nm
72BAR/GIL		20 833.3	Pulse radiolysis and flash photolysis of aqueous solutions in iodate ions; absorption band maximum at 480–490 nm attributed to IO ₂
73TEN/FAR		20 408.2	<i>Transient absorption spectra; maintains that the 490 nm band is related to IO₂ rather than IO (as suggested by 70AMI/TRE); pulse radiolysis technique</i>
81ATH/MOR			EPR spectra in γ -irradiated KIOF ₂ crystals, reassigns spectra originally thought to be IO ₂ F ⁻ to IO ₂
86BYB	0 (B ₁); A ₁ B ₂		EPR spectra; g shifts and excited state parameters, no value given (A ₁ , B ₂ do not necessarily resemble real excited states; photolysis; microwave spectroscopy)
88BYB I ¹⁷ O ₂			EPR spectra, electronic properties closely resemble those of ClO ₂ and BrO ₂
IO₃ 69BAR/GIL		38 461.5–52 631.6	IO ₃ radical not observed under these experimental conditions; absorption spectra; flash photolysis of aqueous solutions of iodate ions
70AMI/TRE		26 315.8	Flash photolysis of IO ₃ ⁻ and IO ⁻ in aqueous solution; absorption spectra in decay kinetics studied by pulse radiolysis; maximum intensity of band structure at 380 nm
70AMI/TRE2		25 316.5	Flash photolysis of IO ₃ ⁻ in boric acid glass; maximum intensity of absorption band at 395 nm
72BAR/GIL		27 777.8	Pulse radiolysis and flash photolysis of aqueous solutions of iodate ions; absorption band maximum at 360 nm attributed to IO ₃
73TEN/FAR IO ₃ (IO ₃) ₂		27 777.8	Transient absorption spectra; though spectra are observed for IO ₃ , the author attributes them to (IO ₃) ₂ ; pulse radiolysis technique
IO₄ 71LES/BAR			Absorption spectra; pulse radiolysis periodate aqueous solutions; IO ₄ proposed as reaction intermediate
I₂O₄ 57SYM			Absorption of IO ⁺ spectra observed from solutions of iodine in concentrated H ₂ SO ₄ ; spectra used as evidence that I ₂ O ₄ is ionic having the structure IO ⁺ IO ₃ ⁻
60DAS/WAD 61WIS/HAN		45 000–85 000 11 049.7; 75 188.0 (9.05 μ m) (13.30 μ m)	Infrared absorption spectra Infrared absorption spectra studies of I ₂ O ₄ in pressed KBr pellets; of the two strong bands, 13.30 μ m is attributed to IO ₃ ⁻ and 9.05 μ m, obtained from stoichiometry, was identified with IO ⁺
69GRU/MUR			Mössbauer spectrum measured at 80 K treating I ₂ O ₄ as absorber; scheme is put forward for the structure of I ₂ O ₄ built of IO groups bound covalently to IO ₃ groups through the O atom
I₂O₅ 61DUR/LEC			*Study of structure by infrared spectroscopy from 2–33 μ m shows existence of I–O–I bridge analogous to that of I ₂ O ₅
70SHE/TUR			Mass spectra studies of I ₂ O ₅ ; author believes earlier studies' peaks assigned to I ₂ O ₅ to be incorrect; evaporation of I ₂ O ₅ only above [280]°C

TABLE 3. (Continued.)

Source	Transition	Energy level (cm ⁻¹)	Comments
I ₂ O ₇ 62MIS/SYM			Ultraviolet spectra at 77 K; no values given; uv spectra at room temperature are irreproducible
I ₄ O ₉ (cr) 85SUN/WRE		15 453.6	Raman spectrometry of crystalline and amorphous solids; formed by gas phase reaction of I ₂ with O ₃ ; I ₄ O ₉ is a distinct molecular species (not a mixture of I ₂ O ₅ and I ₂ O ₄)

TABLE 4. Iodine oxide species (IO): Dissociation energy (D₀^o)

Source	D ₀ ^o (kJ mol ⁻¹)	Temperature	Comments (as reported values)
48COL/GAY	184±21		From graphical Birge-Sponer extrapolation for ground state [X ² Π (ν, 0-12)] D ₀ ^o ; flame spectral data (twelve ground state vibrational levels); 44±5 kcal mol ⁻¹
50HER	183.3		No specific source cited; 1.9 eV
53GAY	183.3±19		Value based on 37VAY, 48COL/GAY; LBX(ν, 0-12); this is supported by extrapolation of upper state and predissociation giving a value of ≤ 1.95 eV; 1.9±0.2 eV
54COT	183.3±19		Value based on 53GAY; Cottrell stated that this value seemed fairly well established; 1.9±0.2 eV
58BRE	184		Value given by Brewer with a “?”; no explanation as to source; 44 kcal mol ⁻¹
58DUR/RAM	176±21		Dissociation energy for ground state is calculated from absorption spectra; a linear Birge-Sponer extrapolation of four upper state vibrational levels yielded 45 kcal mol ⁻¹ ; Birge-Sponer extrapolation was decreased by 10% in analogy with ClO and BrO; 42±5 kcal mol ⁻¹
60DUR/LEG	192±21		Graphical Birge-Sponer extrapolation for A ² Π (ν, 0-5, perturbed) state; predissociation < 2.72 eV; 46±5 kcal mol ⁻¹
61LIP/STE	249.9 or 248.0		Calculated from three- and five-parameter potential functions; 2.59 eV or 2.57 eV
61PHI/SUG	238±25	0 K	D ₀ ^o deduced from the temperature variation of the equilibrium constant; flame photometry; 57±6 kcal mol ⁻¹
62GUR/KHA	184±21		Corresponds to an enthalpy of formation of 40.574±5 kcal mol ⁻¹ value based on data from 48COL/GAY; mentions work of 58DUR/RAM; 44±5 kcal mol ⁻¹
63SCH	183.3±19		D ₀ ^o deduced from 53GAY; 1.9±0.2 eV
65SIN/RAI	239.3		D ₀ ^o calculated from RKR potential energy curves 120 000 cm ⁻¹ , no uncertainty given; 57.2 kcal mol ⁻¹
66VED/GUR	184±21 238±25		L.B.S. for the X ² Π and A ² Π states, assuming that the dissociation limit corresponds to I(² P _{3/2}) + O(¹ D); dissociation equilibria in flames; 44±5 and 57±6 kcal mol ⁻¹
67CAR/DYE	176±21		
68WAG/EVA	177.0	0 K	Based on the spectroscopic measurements of 58DUR/RAM and 60DUR/LEG; 42.3 kcal mol ⁻¹
69BRE/ROS	192±29		Value based on analysis of 48COL/GAY, 58DUR/RAM, and 61PHI/SUG; 46±7 kcal mol ⁻¹
69HER/HUI			Suggests that D ₀ ^o = 238±24 kJ mol ⁻¹ [61PHI/SUG] is compatible with iodine abstraction mechanism but not D ₀ ^o = 174±19 kJ mol ⁻¹ [58DUR/RAM]
70CLY/CRU	176±21; I+O ₃ -IO+O ₂ ; formation of IO(X ² Π) radicals; I(² P _{3/2}) + O ₃ - IO + O ₂ - Δ _r H ^o 298 = -70; *bimolecular disproportionation: IO + IO - IOO + I - 2I + O ₂		D ₀ ^o calculated from linear extrapolation of the upper state (A ² Π) vibrational levels; *rapid bimolecular disproportionation at 293 K occurring through transition state [I-O-O-I]; bond angles are 120°; r distances are O-O=0.15 nm, I-O=0.22 nm, I-O=0.188 nm; the latter value is from 60DUR/LEG

TABLE 4. (Continued.)

Source	D_0° (kJ mol ⁻¹)	Temperature	Comments (as reported values)
70DAR	180 ± 21		Based on 58DUR/RAM, 61PHI/SUG, 62VED/GUR, and 68WAG/EVA; 43 ± 5 kcal mol ⁻¹
72TRI/GOH	183.3 ± 19		Experimental value in agreement with the least-squares fitting of the RKR curve and Hulburt-Hirschfelder value of 44.7; 43.8 ± 4.6 kcal mol ⁻¹
74RAO/RAO	dissociation ($A^2\Pi_{3/2}$): 137.5		Dissociation of upper state calculated by fitting an empirical potential energy curve using Lippencott's three-parameter function and Hulburt-Hirschfelder function with; Franck-Condon factors; r centroids of $A^2\Pi_{2/3}$ - $X^2\Pi_{3/2}$ system; 32.86 kcal mol ⁻¹
75RAD/WHI	222 ± 13	0 K	Reaction in crossed molecular beams of O+ICl led to a measured bond energy value; result based on dissociation energy of ICl; 53 ± 3 kcal mol ⁻¹
79ADD/DON	≥ 210		Kinetics dissociation energy value is consistent with 75RAD/WHI
79HUB/HER	173.7		Based on extrapolations of the vibrational levels of $A^2\Pi_{3/2}$ and the assumption that $A \rightarrow ^2P_{3/2}(\text{Br}) + ^1D(0)$ flame photometry [61PHI/SUG] gives 2.4 eV (less likely as it is as high as BrO); observed predissociation in A gives $D_0^\circ \leq 2.72$ eV; extrapolation of ground state gives 1.94 eV [72TRI/GOH]; 1.8 eV
82BAU/COX	182 ± 21		Derived heat of formation at 298 K to be 172 kJ mol ⁻¹ ; authors refer to the work of [80KER/TRO] whose results have been taken from other sources
83BUS/SIL	230 ± 8		O+Cl reaction in crossed molecular beams; authors preferred a slightly higher IO bond energy value than that proposed by 75RAD/WHI; 55 ± 2 kcal mol ⁻¹
88TYK	atomization: $\Delta_f H^\circ = 181$	25°C	Calculated from reaction trends in log $\Delta_f H^\circ$; trends based on data from JANAF Thermochemical Tables (1985 Supplement) and NBS Tables of Chemical Thermodynamic Properties (1982)
89RED/RAO	249.4 ± 1.7		Estimated from the Lippencott three-parameter potential function; author referred to three other values for the D_0° : 2.4 eV from flame photometry, ≤ 2.74 eV from absorbed predissociation A state, and 1.94 eV from extrapolation of ground state; 59.6 ± 0.4 kcal mol ⁻¹
92MAG/LAV	$\Delta_f H^\circ = 172$		Used value reported by 90DEM/MOL, JPL report mentioned in Introduction; $\Delta_f H^\circ = 41.1$ kcal mol ⁻¹ ; two values given by 89GUR/VEY and 89RED/RAO are mentioned but not used
94RUS/BER	201.2 ± 21		Roughly the mean of the preferred values of 75RAD/WHI and 68GAY; 50 ± 5 kcal mol ⁻¹
95MON/STI	226		Use of photoionization efficiency spectra
96GIL/TUR	$\Delta_f H^\circ < 120.5$		Determined rate constants for the reaction $\text{O}(^3P)$ with alkyl iodides; suggested $\Delta_f H^\circ$ (IO, 298 K) < 28.8 kcal mol ⁻¹

TABLE 5. Iodine oxide species: Structures and vibrational frequencies

Source	Structure	Bond distance X-Y (Å)	Vibrational frequencies (cm ⁻¹)	Comments
IO				
37VAI				Vibrational analysis; ω_e and $\omega_e x_e$ values given
80LOE/MIL				Vibrational analysis; ω_e and $\omega_e x_e$ values given
IO ₂				
60DAS/WAD	IO ₂ (complex iodates) IO ₂ (iodoxy benzenes)			Spectrum interpreted in terms of a network of IO ₃ groups and polymerized ion chains; IO symmetric and antisymmetric stretching frequencies are estimated by trends in many iodine compounds

TABLE 5. (Continued.)

Source	Structure	Bond distance X-Y (Å)	Vibrational frequencies (cm ⁻¹)				Comments
IO₃							
60DUV/LEC			ν_1 (sym.) 745	ν_2 420	ν_3 (asym.) 855; 850	Absorption spectra of I ₂ O ₅ ; the three vibrational frequencies given were assumed to represent the IO ₂ fragment of I ₂ O ₅	
86BYB	C _{2v} point group					Observation and calculation of EPR spectrum of structure in KClO ₄ crystal	
88BYB I ¹⁷ O ₂	C _{2v} point group					EPR spectra interpreted in terms of bond angle of 118°; no bond distances given	
92GIL/POL			ν_1 765±25	ν_2 192±35		Photoelectron spectroscopy	
56VEN/SUN	Pyramidal C _{3v} point group	1.79	A ₁ (sym.) 357 780		E(asym.) 326 809	Raman effect data; type E frequencies are doubly degenerate; observed interbond angles and observed frequencies are presumably taken from Landolt-Bornstein Tables 1951 (data could not be found in this publication); X-Y distances calculated by Badger's rule; force constants given; I-O-I bond angle is 89°	
64RAO/SAN	Pyramidal C _{3v} point group					Identifies vibrational frequencies: two symmetrical (A ₁) and two doubly degenerate E modes but no values given; uses 56VEN/SUN values to calculate mean square amplitudes	
72RAO	Pyramidal C _{3v} point group					Identifies XY ₃ pyramidal type molecule with six vibrations (two symmetric A ₁ and two doubly degenerate E modes) but no values given; calculations based on 56VEN/SUN; calculation of centrifugal distortion constants	
78THI/MOH	Pyramidal C _{3v} point group		ν_2 (A ₂) 357	ν_1 (A ₁) 780	ν_4 (E) 362	ν_3 (E) 809	Group theoretical method; force constants given; frequencies and structure presumably taken from Landolt-Bornstein tables; authors cite origin of data in three references which do not deal with IO ₃
I₂O							
60DUV/LEC	IOI		ν_1 597	ν_2 170	ν_3 688	Absorption spectra of I ₂ O ₅ ; frequencies given for I ₂ O but no indication as to origin of these values	
I₂O₂							
30BRA	IOOI or OIIO					Established existence as an intermediate in the equilibrium involving I ₃ O ₂ ⁻ and H ₂ X ₂ O ₃	
I₂O₄							
50WIL/DHA	Nonhygroscopic; (IO ⁺ ₃ IO ₃ ⁻); diamagnetic					Monomeric IO ₂ unit does not occur in solid state; stable compound at room temperature; assumed structure	
57SYM	Diamagnetic; IO ⁺ IO ₃ ⁻					Absorption spectra; structure and diamagnetic attribute based on 50WIL/DHA observations	
60DAS/WAD			ν_1 622 s 658 m	ν_2 408	ν_{3a} 825 w 783 s ν_{3b} 745 s	I-O-I 578 s	Ultraviolet absorption spectrum interpreted in terms of a network of IO ₃ groups and polymerized IO chains; spectra estimated in analogy to TeO frequency of 796 cm ⁻¹
61WIS/HAN	IO ⁻ IO ₃ ⁻					Structure determination from infrared spectra	
63DAS/WAD	Diamagnetic					Infrared spectrum in Nujol mulls and structure: critique of earlier work by Wise and Hannan, Dassent and Waddington (1960); I ₂ O ₄ spectrum explained in terms of polymerized I-OI chains and IO ₃ groups	
69GRU/MUR						Mössbauer study of the structure of the oxide; conclusions: there are two sterically and chemically inequivalent states of iodine; there is no undeformed IO ₃ ⁻ ion	
70GRU/LUR	Nonionic					Mössbauer study of I ₂ O ₄ in MgTeO ₄ at liquid nitrogen temperature; proposes a new electronic structure for I ₂ O ₄ ; symmetry is close to that of IO ₃ in HIO ₃ and an IO group	
75JON	OIOIO ₂ (IO ⁻ IO ₃ ⁻)					Determination of structure; Mössbauer studies; confirms Grushko's work	
76DAL/CAR	OIOIO ₂					Infrared spectra, partial Raman spectra; *vibrational frequency stretching of solid state from 900-550 cm ⁻¹ but no assignment made; structure of I ₂ O ₄ is similar to I ₂ O ₅	

TABLE 5. (Continued.)

Source	Structure	Bond distance X-Y (Å)	Vibrational frequencies				Comments
I₂O₅							
81ELL/WOL	Centrosymmetric O-I-O-IO ₂	*					Infrared and Raman spectroscopy of crystal; 5 infrared and 3 Raman bands were observed between 830 and 735 cm ⁻¹ for the I=O stretch, and 9 ir and 6 Raman bands between 670 and 400 cm ⁻¹ are possible for I-O stretch but no assignments are made; discussion of structural models; partial force constants given
87LEH/CHR	(P2 ₁ /c) space group						Crystal structure determination by pattern decomposition and Rietveld method on synchrotron x ray
55KOJ/TSU						Nuclear quadrupole data	
57DUV			ν_1 804		ν_3 755	1160	Infrared absorption spectra with rapid dissociation and sublimation at 410°; vibrational frequencies are based on earlier interpretations
60DUV/LEC	C _{2v} IO ₂ -O-IO ₂		ν_1 (sym.) 804;835	ν_2 (asym.) 355	ν_3 758;743	ν_4 x	Absorption spectra; redefinition of structure is symmetrical ν_3 is doubly degenerate and ν_4 was not measured; *supplementary bands are due to the existence of the acid function
70SEL/KJE	Two IO ₃ pyramids O ₂ I-O-IO ₂	Intramolecular and interatomic distances and angles given					Monoclinic crystal structure studies of crystalline compound; authors disagree with 60DUV/LEC C _{2v} symmetry attributed to I ₂ O ₅
73SEM/MOS	Crystal symmetry of P2 ₁ /c (monoclinic)						X-ray spectrum of solid I ₂ O ₅
76DAL/CAR		I-O-I *1.77-1.83 *1.92-1.95					Infrared spectra, partial Raman spectra; *bond length—see 70SEL/KJE
81ELL/WOL	O ₂ -I-O-IO ₂ (quasi- monomeric)				*		Infrared and Raman spectroscopy of crystal; *I-O-I stretch vibrations of bands 610-400 cm ⁻¹ , 12 infrared bands observed between 850 and 670 cm ⁻¹ attributed to I=O stretch, four I-O-I bending modes attributed to bands around 100 cm ⁻¹ but no assignment made; discussion of structural models; partial force constants given
I₂O₆							
77SIE/WEI	IO ₂ ⁺ IO ₄ ⁻						Existence of I ₂ O ₆ is confirmed, according to Raman spectra and vibrational frequencies; diamagnetism proves mixed valence iodine; the compound is described as an iodyl periodate
I₄O₆							
85SUN/WRE					*		*Raman spectra of amorphous solid at room temperature observed and tentative assignments made: strong Raman bands at 800 cm ⁻¹ attributed to I=O stretch, bands in frequency range 400-500 cm ⁻¹ attributed to I-O stretch, and the band at 692 cm ⁻¹ is assigned to O-I=O symmetric stretch; confirms I ₄ O ₆ existence

6. NIST-JANAF Thermochemical Tables

NIST-JANAF Thermochemical Tables for IO(g) (Sec. 6.1), OIO(g) (Sec. 6.2), IOO(g) (Sec. 6.3), IO₃(g) (Sec. 6.4), IOI(g) (Sec. 6.5), and IIO(g) (Sec. 6.6) are presented on the following pages.

I₂(g)

Iodine oxide (OIO)

M_r = 158.90327

T/K	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = P ^o = 0.1 MPa		log K _r
	C _p ^o /J·K ⁻¹ ·mol ⁻¹	S ^o /J·K ⁻¹ ·mol ⁻¹	H ^o -H ^o (T _r)/kJ·mol ⁻¹	ΔH ^o /kJ·mol ⁻¹	
0	0.000	0.000	INFINITE	162.744	INFINITE
50	34.278	211.198	114.979	162.490	-167.564
100	37.850	236.126	319.929	158.563	-82.825
150	40.093	251.918	394.779	161.091	-54.707
200	42.280	263.746	385.600	160.427	-40.709
250	44.599	273.429	382.225	159.828	-32.344
298.15	46.697	281.468	381.468	159.323	-26.959
300	46.772	281.757	381.468	159.304	-26.787
400	50.184	295.711	383.348	150.373	-19.908
500	52.445	307.170	387.000	128.355	-16.203
600	53.929	316.872	391.191	128.642	-13.966
700	54.929	325.265	395.473	128.950	-12.364
800	55.626	332.648	399.668	129.253	-11.160
900	56.127	339.230	403.705	129.542	-10.221
1000	56.498	345.164	407.559	129.811	-9.469
1100	56.779	350.562	411.226	130.059	-8.852
1200	56.997	355.513	414.714	130.283	-8.336
1300	57.168	360.018	418.048	130.486	-7.906
1400	57.306	364.324	421.187	130.677	-7.539
1500	57.419	368.281	424.187	130.779	-7.220
1600	57.511	371.990	427.069	130.870	-6.915
1700	57.588	375.479	429.815	130.915	-6.664
1800	57.653	378.773	432.444	130.911	-6.440
1900	57.709	381.891	434.965	130.855	-6.240
2000	57.756	384.853	437.386	130.745	-6.061
2100	57.797	387.672	439.714	130.583	-5.898
2200	57.832	390.361	441.955	130.371	-5.751
2300	57.863	392.933	444.116	130.113	-5.616
2400	57.891	395.396	446.202	129.813	-5.493
2500	57.915	397.760	448.217	129.476	-5.380
2600	57.936	400.031	450.167	129.109	-5.276
2700	57.955	402.216	452.054	128.716	-5.180
2800	57.972	404.316	453.884	128.300	-5.091
2900	57.988	406.361	455.659	127.887	-5.009
3000	58.002	408.327	457.382	127.458	-4.933
3100	58.014	410.229	459.056	127.026	-4.861
3200	58.026	412.071	460.684	126.596	-4.794
3300	58.036	413.857	462.268	126.172	-4.732
3400	58.046	415.590	463.811	125.756	-4.673
3500	58.055	417.272	465.315	125.351	-4.618
3600	58.063	418.908	466.781	124.959	-4.566
3700	58.070	420.499	468.211	124.581	-4.517
3800	58.077	422.048	469.608	124.219	-4.471
3900	58.083	423.555	470.972	123.874	-4.427
4000	58.089	425.027	472.305	123.546	-4.386
4100	58.094	426.461	473.608	123.234	-4.347
4200	58.099	427.857	474.884	122.937	-4.310
4300	58.104	429.228	476.131	122.663	-4.274
4400	58.108	430.564	477.353	122.402	-4.240
4500	58.112	431.870	478.550	122.156	-4.208
4600	58.116	433.147	479.724	121.926	-4.177
4700	58.120	434.397	480.874	121.709	-4.147
4800	58.123	435.621	482.001	121.505	-4.119
4900	58.126	436.819	483.108	121.313	-4.092
5000	58.129	437.994	484.194	121.132	-4.067
5100	58.132	439.145	485.260	120.959	-4.042
5200	58.135	440.274	486.307	120.795	-4.018
5300	58.137	441.381	487.336	120.636	-3.995
5400	58.140	442.465	488.347	120.481	-3.973
5500	58.142	443.535	489.341	120.333	-3.952
5600	58.144	444.592	490.318	120.184	-3.931
5700	58.146	445.633	491.276	120.042	-3.911
5800	58.148	446.652	492.224	119.896	-3.893
5900	58.150	447.617	493.155	119.733	-3.875
6000	58.151	448.594	494.071	119.575	-3.857

PREVIOUS:

CURRENT: March, 1996 (1 bar)

Ideal Gas

Iodine oxide (OIO)

$$\Delta_f H_f^{\circ}(0 \text{ K}) = [438 \pm 25] \text{ kJ} \cdot \text{mol}^{-1}$$

$$S^{\circ}(298.15 \text{ K}) = [281.5 \pm 4] \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_f H_f^{\circ}(0 \text{ K}) = [162.7 \pm 25] \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_f H_f^{\circ}(298.15 \text{ K}) = [159.3 \pm 25] \text{ kJ} \cdot \text{mol}^{-1}$$

Electronic Level and Quantum state	ϵ_i , cm ⁻¹	Quantum Weight g_i
X ² B ₁	0.0	2

Vibrational Frequencies and Degeneracies

ν_1 , cm ⁻¹	765(1)
	192(1)
	800(1)

Point Group: C_{2v}

Bond Distance: I-O = [1.8] Å

Bond Angle: O-I-O = [120]°

Product of the Moments of Inertia: I_AI_BI_C = 10⁻¹⁷ g³cm⁶

σ = 2

Enthalpy of Formation

For the series OXO(g) [where X = F, Cl, Br, I], there are only reliable experimental data for OClO(g). Assuming that the values D₀(ClO) and Δ_fH_f^o(OClO,g) are reasonable, we adopt the ratio of the numbers (~1.94) to apply for a similar relationship between IO(g) and OIO(g). Thus, Δ_fH_f^o(OIO,g, 0 K) = 1.94 D₀(IO) = 438 kJ·mol⁻¹.

Heat Capacity and Entropy

Based on the ESR study by Byberg,¹ the ground state of the free IO₂ molecule belongs to the representation B₁ of the point group C_{2v}. This symmetric, bent molecule is estimated to have an G-I-O angle of [120]° and a bond length of [1.8] Å in analogy with the corresponding fluorine, chlorine, and bromine oxide molecules.² The principal moments of inertia in g cm² are: I_A = 3.4373 × 10⁻³⁹, I_B = 12.1991 × 10⁻³⁹, and I_C = 16.3491 × 10⁻³⁹. Two of the three vibrational frequencies have been derived by Gilles *et al.*,³ who used photoelectron spectroscopic techniques; ν₁ is estimated based on anticipated trends with the OXO(g) family⁴ and assuming ν₂ > ν₃.

References

- J. R. Byberg, *J. Chem. Phys.* **88**(4), 2129-34 (1988).
- NIST-JANAF Thermochemical Tables: OFO(g); Sept. 1995; OCO(g); March 1996; OBrO(g); March 1996.
- M. K. Gilles, M. L. Polak, and W. C. Lineberger, *J. Chem. Phys.* **96**(11), 8012-20 (1992).

Iodine oxide (OIO)

I₂(g)

IO₂(g)

Iodine oxide (IOO)

Ideal Gas

Iodine oxide (IOO)

$\Delta_f H^\circ(0 \text{ K}) = [119 \pm 40] \text{ kJ mol}^{-1}$
 $\Delta_f H^\circ(298.15 \text{ K}) = [116.5 \pm 40] \text{ kJ mol}^{-1}$

T/K	C _p ^o	S ^o - [C _p ^o - R ln(T ₀ /T)]/T	H ^o - H ^o (T ₀)	Δ _f H ^o	log K _f
0	.000	INFINITE	-12.806	119.000	INFINITE
50	35.573	219.838	44.181	118.725	-121.430
100	41.565	246.433	338.245	118.195	-39.512
150	45.076	264.029	310.732	117.715	-38.710
200	46.779	273.746	291.172	117.359	-38.771
250	47.962	281.859	276.374	117.089	-38.771
298.15	48.727	296.374	256.374	116.862	-38.771
300	48.754	296.676	256.375	116.857	-18.557
350	51.463	310.965	184.405	116.671	-10.948
400	51.463	322.225	101.118	116.589	-9.457
450	51.620	331.177	52.778	116.528	-9.457
500	51.620	337.401	31.478	116.486	-8.389
600	54.355	347.110	316.568	116.199	-7.387
700	54.355	353.549	318.548	116.950	-6.962
800	55.467	359.368	323.444	116.254	-6.461
900	55.863	364.674	325.954	117.402	-6.050
1000	56.184	369.548	329.387	118.107	-5.707
1200	56.446	374.056	332.852	118.808	-5.416
1300	56.662	378.248	335.761	119.481	-5.167
1400	56.842	382.163	338.725	120.126	-4.951
1500	56.993	385.837	341.536	120.742	-4.761
1600	57.121	389.296	344.263	121.327	-4.594
1700	57.234	392.564	346.854	121.881	-4.447
1800	57.324	395.661	349.335	122.404	-4.313
1900	57.400	398.603	351.735	122.897	-4.193
2000	57.475	401.406	354.034	123.361	-4.086
2100	57.537	404.081	356.248	123.796	-3.988
2200	57.591	406.640	358.384	124.204	-3.899
2300	57.639	409.092	360.446	124.588	-3.818
2400	57.681	411.446	362.439	124.946	-3.743
2500	57.719	413.709	364.368	125.280	-3.675
2600	57.753	415.888	366.236	125.592	-3.612
2700	57.784	417.988	368.047	125.884	-3.553
2800	57.812	419.999	369.804	126.158	-3.499
2900	57.836	421.977	371.511	126.416	-3.449
3000	57.856	423.874	373.169	126.658	-3.403
3100	57.880	425.711	374.789	126.885	-3.359
3200	57.899	427.492	376.353	127.098	-3.319
3300	57.916	429.221	377.883	127.298	-3.281
3400	57.932	430.900	379.374	127.484	-3.245
3500	57.946	432.532	380.828	127.656	-3.211
3600	57.960	434.120	382.247	127.815	-3.180
3700	57.972	435.666	383.632	127.962	-3.150
3800	57.983	437.172	384.986	128.098	-3.122
3900	57.994	438.640	386.309	128.224	-3.096
4000	58.004	440.072	387.603	128.340	-3.070
4100	58.013	441.470	388.869	128.446	-3.047
4200	58.021	442.836	390.108	128.543	-3.024
4300	58.029	444.169	391.322	128.631	-3.004
4400	58.036	445.474	392.511	128.711	-2.982
4500	58.044	446.749	393.676	128.783	-2.962
4600	58.051	447.998	394.819	128.848	-2.943
4700	58.057	449.220	395.939	128.906	-2.926
4800	58.063	450.417	397.039	128.958	-2.908
4900	58.068	451.590	398.118	129.004	-2.892
5000	58.073	452.740	399.178	129.044	-2.876
5100	58.078	453.868	400.219	129.079	-2.861
5200	58.083	454.974	401.242	129.110	-2.847
5300	58.087	456.060	402.247	129.136	-2.833
5400	58.091	457.126	403.235	129.158	-2.820
5500	58.095	458.172	404.207	129.176	-2.807
5600	58.099	459.201	405.162	129.191	-2.794
5700	58.103	460.214	406.100	129.203	-2.782
5800	58.105	461.204	407.018	129.212	-2.771
5900	58.109	462.181	407.919	129.218	-2.760

PREVIOUS: CURRENT: March 1996 (I, bar)

Electronic Level and Quantum Weight state, ϵ_e , cm⁻¹, g_v, [2]

Vibrational Frequencies, and Degeneracies, ν , cm⁻¹, [1500](1), [1500](1), [275](1)

Point Group: C_{2v}; L-O = [2.41] Å; O-O = [1.25] Å

Bond Distance: L-O = [2.01] Å; O-O = [1.25] Å

Bond Angle: L-O-O = [120]°

Product of the Moments of Inertia: $I_A I_B I_C = [1314.2931 \times 10^{-117}] \text{ g}^3 \text{ cm}^6$

$\sigma = 1$

Enthalpy of Formation

Following trends in the reaction $\text{XOO(g)} \rightarrow \text{X(g)} + 2\text{O(g)}$, a reasonable estimate for the iodine reaction would be $\Delta_f H^\circ(0 \text{ K}) = -91.25 \text{ kJ mol}^{-1}$. However, looking at the trends in the reaction $\text{XOO(g)} \rightarrow \text{XO(g)} + \text{O(g)}$, a reasonable estimate for the iodine reaction would be 260 kJ mol^{-1} , which leads to a $\Delta_f H^\circ(0 \text{ K}) = 119 \text{ kJ mol}^{-1}$. This large discrepancy in estimates is a result of the estimates and uncertainties in all XOO enthalpies of formation. We adopt the value based on the reaction involving an X-O bond breakage.

Heat Capacity and Entropy

The vibrational frequencies and structure are estimated based on the existing data for FOO(g) , ClOO(g) , and BrOO(g) .¹ The principal moments of inertia in g cm² are: $I_A = 1.1391 \times 10^{-39}$, $I_B = 33.4021 \times 10^{-39}$, and $I_C = 34.3412 \times 10^{-39}$.

References

¹NIST-JANAF Thermochemical Tables: FOO(g) , Spt. 1995; ClOO(g) , March 1996; BrOO(g) , March 1996.

Iodine oxide (IOI) $M_r = 269.80834$ **Iodine oxide (IOI)** **I₂O(g)**

$\Delta_f H^\circ(0 \text{ K}) = 348 \pm 25 \text{ kJ}\cdot\text{mol}^{-1}$ $\Delta_f H^\circ(0 \text{ K}) = [124 \pm 25] \text{ kJ}\cdot\text{mol}^{-1}$ $\Delta_f H^\circ(298.15 \text{ K}) = [119.5 \pm 25] \text{ kJ}\cdot\text{mol}^{-1}$

$S^\circ(298.15 \text{ K}) = [308.1 \pm 4] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

T/K	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p ^o = 0.1 MPa		log K _r
	C _p	S ^o - [G ^o - H ^o (T _r)]/T	H ^o - H ^o (T _r)	$\Delta_f H^\circ$	
0	0.000	INFINITE	-13.025	124.000	INFINITE
50	37.610	230.650	455.463	124.000	-123.241
100	40.943	257.873	351.050	123.256	-58.598
150	44.200	275.070	323.013	122.204	-37.221
200	47.472	288.246	312.734	121.328	-26.621
250	50.053	299.151	308.955	120.322	-20.310
298.15	51.874	308.111	306.111	119.485	-16.264
300	51.933	308.432	306.112	119.453	-16.135
350	54.269	323.727	312.181	101.652	-11.042
400	55.587	335.988	314.157	57.423	-8.834
600	56.302	346.187	318.670	57.684	-7.832
700	56.780	354.905	323.239	57.945	-7.113
800	57.100	362.209	327.682	58.193	-6.572
900	57.324	368.249	331.945	58.430	-6.104
1000	57.487	375.297	335.972	58.630	-5.809
1100	57.608	380.792	339.801	58.835	-5.530
1200	57.701	385.799	343.428	59.033	-5.297
1300	57.774	390.420	346.867	59.160	-5.099
1400	57.832	394.704	350.133	59.187	-4.930
1500	57.879	398.695	353.239	59.224	-4.782
1600	57.918	402.432	356.198	59.264	-4.653
1700	57.950	405.944	359.022	59.115	-4.540
1800	57.977	409.258	361.722	58.953	-4.439
1900	58.000	412.393	364.307	58.712	-4.349
2000	58.019	415.368	366.786	58.351	-4.269
2100	58.036	418.200	369.167	57.953	-4.196
2200	58.051	420.898	371.458	57.523	-4.131
2300	58.064	423.484	373.672	57.068	-4.074
2400	58.075	425.952	375.792	56.599	-4.018
2500	58.085	428.323	377.846	56.124	-3.969
2600	58.094	430.601	379.831	55.100	-3.925
2700	58.101	432.794	381.753	54.414	-3.884
2800	58.108	434.907	383.613	53.720	-3.847
2900	58.115	436.946	385.418	53.077	-3.812
3000	58.120	438.916	387.168	52.347	-3.781
3100	58.125	440.822	388.868	51.688	-3.752
3200	58.130	442.668	390.521	51.038	-3.725
3300	58.134	444.457	392.128	50.402	-3.699
3400	58.138	446.191	393.695	49.787	-3.676
3500	58.142	447.877	395.217	49.197	-3.654
3600	58.145	449.515	396.703	48.634	-3.634
3700	58.148	451.109	398.152	48.092	-3.614
3800	58.151	452.659	399.566	47.574	-3.597
3900	58.153	454.170	400.947	47.083	-3.580
4000	58.156	455.642	402.296	46.615	-3.564
4100	58.158	457.078	403.615	46.169	-3.549
4200	58.160	458.480	404.904	45.745	-3.534
4300	58.162	459.848	406.166	45.341	-3.521
4400	58.164	461.185	407.401	44.957	-3.508
4500	58.165	462.493	408.611	44.592	-3.495
4600	58.167	463.771	409.797	44.247	-3.483
4700	58.168	465.022	410.958	43.921	-3.472
4800	58.169	466.246	412.096	43.613	-3.461
4900	58.171	467.446	413.215	43.323	-3.451
5000	58.172	468.621	414.311	43.050	-3.440
5100	58.173	469.773	415.387	42.793	-3.430
5200	58.174	470.903	416.444	42.551	-3.421
5300	58.175	472.011	417.482	42.323	-3.412
5400	58.176	473.098	418.502	42.109	-3.403
5500	58.177	474.166	419.504	41.909	-3.394
5600	58.178	475.214	420.490	41.722	-3.386
5700	58.179	476.244	421.459	41.547	-3.378
5800	58.180	477.256	422.412	41.384	-3.370
5900	58.181	478.250	423.350	41.232	-3.362
6000	58.181	479.228	424.274	41.091	-3.354

CURRENT: March 1996 (I bar)

PREVIOUS:

Iodine oxide (IOI)

$\Delta_f H^\circ(0 \text{ K}) = 348 \pm 25 \text{ kJ}\cdot\text{mol}^{-1}$
 $S^\circ(298.15 \text{ K}) = [308.1 \pm 4] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

Electronic Level and Quantum Weight state	ϵ_n , cm ⁻¹	Weight g _n
X/A	0.0	1

Vibrational Frequencies and Degeneracies	
ν , cm ⁻¹	ν , cm ⁻¹
[475](1)	
[100](1)	
[325](1)	

Point Group: C_{2v}
 Bond Distance: I-O = [2.01] Å
 Bond Angle: F-O-I = [115]°
 Product of the Moments of Inertia: I_AI_BI_C = 42498.6720 × 10⁻¹¹⁷ g³cm⁶
 $\sigma = 2$

Enthalpy of Formation
 For the series XO(g) [where X = F, Cl, Br, I], there are only reliable experimental data for ClO(g). Assuming that the values D₀(ClO) and $\Delta_f H^\circ(\text{ClOCl})_g$ are reasonable, we adopt the ratio of the numbers (1.52) to apply for a similar relationship between IO(g) and IOI(g). The ratio for the corresponding bromine oxides is approximately 1.6.

Heat Capacity and Entropy
 The structure of this molecule is estimated to be bent with a I-O-I angle of [115]°, and a bond length of [2.01] Å in analogy with the corresponding fluorine, chlorine, and bromine oxide molecules. The principal moments of inertia in g cm² are I_A = 2.8860 × 10⁻³⁹, I_B = 119.9153 × 10⁻³⁹, and I_C = 122.8013 × 10⁻³⁹. The vibrational frequencies are estimated from known frequencies of FOF(g), ClOC(g), and BrOB(g) and expected trends in this halogen oxide family.

References
 NIST-JANAF Thermochemical Tables: FOF(g): Sept. 1995; ClOC(g): March 1996; BrOB(g): March 1996.

I₂O(g)

Iodine oxide (IIO)

Ideal Gas

Iodine oxide (IIO)

Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p° = 0.1 MPa	
T/K	C _p ^o / J·K ⁻¹ ·mol ⁻¹	H° - H°(T _r) / kJ·mol ⁻¹	ΔG° / kJ·mol ⁻¹
0	0.000	INFINITE	INFINITE
50	39.124	-13.691	110.500
100	45.462	-11.942	103.624
150	47.981	-9.800	96.926
200	49.683	-7.458	89.611
250	51.153	-5.015	80.611
298.15	52.359	-2.493	70.520
300	52.401	-2.493	70.520
350	54.230	-1.997	62.702
400	55.386	-1.435	54.535
450	55.961	-0.848	46.189
500	56.127	-0.251	37.702
550	56.620	0.344	29.127
600	56.961	0.942	20.500
650	57.203	1.535	11.872
700	57.384	2.122	3.279
750	57.520	2.702	-5.337
800	57.619	3.272	-12.838
850	57.683	3.833	-20.273
900	57.717	4.385	-27.644
950	57.731	4.928	-34.956
1000	57.731	5.462	-42.219
1100	57.707	6.584	-53.454
1200	57.663	7.702	-64.566
1300	57.601	8.815	-75.556
1400	57.523	9.923	-86.427
1500	57.430	11.026	-97.181
1600	57.324	12.124	-107.820
1700	57.207	13.217	-118.346
1800	57.080	14.305	-128.761
1900	56.944	15.388	-139.068
2000	56.800	16.466	-149.268
2100	56.648	17.540	-159.363
2200	56.490	18.610	-169.355
2300	56.327	19.676	-179.245
2400	56.160	20.739	-189.034
2500	56.000	21.798	-198.733
2600	55.838	22.854	-208.343
2700	55.675	23.907	-217.864
2800	55.511	24.957	-227.297
2900	55.346	26.004	-236.643
3000	55.180	27.048	-245.902
3100	55.013	28.089	-255.074
3200	54.845	29.127	-264.160
3300	54.676	30.162	-273.162
3400	54.506	31.194	-282.081
3500	54.335	32.223	-290.917
3600	54.163	33.250	-299.671
3700	53.990	34.274	-308.343
3800	53.817	35.295	-316.934
3900	53.643	36.313	-325.445
4000	53.468	37.328	-333.877
4100	53.292	38.340	-342.230
4200	53.115	39.349	-350.504
4300	52.937	40.355	-358.700
4400	52.758	41.358	-366.818
4500	52.578	42.358	-374.858
4600	52.397	43.355	-382.820
4700	52.215	44.349	-390.704
4800	52.032	45.340	-398.511
4900	51.848	46.328	-406.241
5000	51.663	47.313	-413.894
5100	51.477	48.295	-421.470
5200	51.290	49.274	-428.970
5300	51.102	50.250	-436.394
5400	50.913	51.223	-443.743
5500	50.723	52.193	-451.017
5600	50.532	53.160	-458.217
5700	50.340	54.124	-465.343
5800	50.147	55.085	-472.395
5900	49.953	56.043	-479.373
6000	49.758	57.000	-486.277

$S^{\circ}(298.15 \text{ K}) = [330.6 \pm 4] \text{ J K}^{-1} \text{ mol}^{-1}$
 $\Delta H_f^{\circ}(0 \text{ K}) = [110.5 \pm 40] \text{ kJ mol}^{-1}$
 $\Delta H_f^{\circ}(298.15 \text{ K}) = [106.7 \pm 40] \text{ kJ mol}^{-1}$

Electronic Level and Quantum state	Weight
[1 ⁺ A ⁺]	0.0

Vibrational Frequencies and Degeneracies

[750](1)	
[100](1)	
[170](1)	

Point Group: C_{2v}
 Bond Distances: I-O = [1.9] Å; I-I = [3.0] Å
 Bond Angle: I-O-I = [125]°
 Product of the Moments of Inertia: I_AI_BI_C = 6753.8, 6868 × 10⁻¹¹⁷ g³cm⁶
 $\sigma = 1$

Enthalpy of Formation
 For the four halogen oxide species, XXO(g) where X = F, Cl, Br, I, there are no experimental data related to the enthalpy of formation. Thus the enthalpy of formation is estimated based on assumption that the X-X bond in XXO(g) is 0.6 D₂(X₂). This leads to a $\Delta H_f^{\circ}(\text{IIO}, 0 \text{ K}) = 110.5 \text{ kJ mol}^{-1}$.

Heat Capacity and Entropy
 The structure of this molecule is estimated to be bent with a I-I-O angle of [125]° and bond distances r(I-I) = [3.0] Å and r(I-O) = [1.9] Å. This structure is estimated in analogy with the corresponding chlorine and bromine molecules. The vibrational frequencies are estimated from the known frequencies of ClClO and BrBrO. The principal moments of inertia in g²cm² are: I_A = 5.1010 × 10⁻³⁹, I_B = 112.5438 × 10⁻³⁹, and I_C = 117.6448 × 10⁻³⁹.

References
 NIST-JANAF Thermochemical Tables: ClClO(g), March 1996; BrBrO(g); March 1996.

I₂O(g)

Iodine oxide (IIO)

Ideal Gas

Iodine oxide (IIO)

7. Conclusions

Of the iodine oxides mentioned in the literature, only five have been isolated and (at least, partially) characterized: IO(g), OIO(g), I₂O₄(cr), I₂O₅(cr), I₄O₉(cr). Only early studies mention I₆O₁₃ and I₁₀O₁₉; it would appear that these species do not exist. IO₃ and IO₄ are proposed as intermediates in solutions or crystalline environments, with only an absorption maximum as a characterization. The other species are proposed to exist but there are no definitive studies as to their isolation and characterization.

In Table 6, a summary of the recommended thermodynamic properties at ambient conditions for six gaseous iodine oxides (IO, OIO, IOO, IO₃, IOI, IIO) are given. Even though there is a severe lack of experimental or calculational data for these six iodine oxides, tables are being generated for these species to match the corresponding fluorine, chlorine, and bromine oxides. The brackets indicate estimated values. *The recommended values contain significant uncertainties. In all cases, experimental enthalpy of formation data are needed. However, the prime effort should be directed at confirming the dissociation energy of IO(g) and determining the enthalpy of formation of OIO(g). Further efforts should be directed towards establishing the enthalpy of formation for the remaining four gaseous species. For any of the polyatomic gaseous species (except OIO), spectroscopic measurements for the geometry and vibrational frequencies would greatly reduce the uncertainties in the resulting thermal functions. For OIO(g), two of the three vibrational frequencies have been observed experimentally.*

TABLE 6. Thermodynamic properties of the iodine oxides

Compound	0 K		298.15 K		
	$\Delta_f H^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹	$\Delta_f G^\circ$ kJ mol ⁻¹	C_p° J K ⁻¹ ·mol ⁻¹	S° J K ⁻¹ ·mol ⁻¹
IO(g)	130.0±13	128±13	106.5	32.9	239.6±1
OIO(g)	[162.7±25]	[159.3±25]	[153.9]	[46.7]	[281.5±4]
IOO(g)	[119±40]	[116.5±40]	[106.6]	[48.7]	[296.4±4]
IO ₃ (g)	[248±50]	[241.9±50]	[263.6]	[61.6]	[293.0±4]
IOI(g)	[124±25]	[119.5±25]	[92.8]	[51.9]	[308.1±4]
IIO(g)	[110.5±40]	[106.7±40]	[73.3]	[52.4]	[330.6±4]

The main thrust in this study of the iodine oxygen system is to verify the existence of the various iodine oxygen species and to obtain spectroscopic data for them. Additional confirmation is needed as to the existence of the condensed phases, although this is a much lower priority. There seems to be little demand for heat capacity and enthalpy measurements at this time.

Note added. After this article was accepted for publication, two additional references on the dissociation energy of IO(g) were brought to our attention:

- $D_0^\circ(\text{IO})=234\pm 5 \text{ kJ mol}^{-1}$, $\Delta_f H^\circ=120\pm 5 \text{ kJ mol}^{-1}$ an *ab initio* calculation by P. H. Hassanzadeh, K. K. Ira-

kura and R. D. Johnson III, private communication.

- $D_0^\circ(\text{IO})=219\pm 4 \text{ kJ mol}^{-1}$, $\Delta_f H^\circ=135\pm 4 \text{ kJ mol}^{-1}$ a quantum mechanical calculation by M. P. McGrath and F. S. Rowland, *J. Phys. Chem.* **100**, 4815 (1996).

8. Acknowledgments

This work was undertaken as part of a larger study to provide JANAF Thermochemical Tables for as many halogen oxide species as possible. This particular study for the iodine 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. The contribution of Stanley Abramowitz in discussions on the spectroscopic properties of the triatomic molecules is greatly appreciated; appreciation is also extended to R. B. Klemm (Brookhaven National Laboratory) and A. R. Ravishankara (NOAA) for information pertaining to the enthalpy of formation of IO. Appreciation is also extended to Karl Irikura (NIST) for providing us with a calculated value for the dissociation energy of IO and providing comments on the text. The IO thermal function calculations were performed by David Neumann.

9. References—Annotated Bibliography

The following articles are a combination of all references dealing with the iodine 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-U.S.) have not been obtained and read.

- 1845MIL M. E. Millon, "Action of sulfuric acid on iodic acid and the compounds that result," *Ann. Chim. Phys.* **12**, 345 and 353 (1844); *J. Prakt. Chem.* **34**, 321 and 337 (1845); preparation (partial hydrolysis of iodine nitrate or iodine sulfate).
- 1861KAE H. Kaemmerer, "Research on some iodine compounds," *J. Prakt. Chem.* **83**, 65 (1861); preparation, reaction and general reference.
- 1870DIT A. Ditte, *C. R. Acad. Sci.* **70**, 1935 (1870); heat of formation.
- 1878BER M. Berthelot, "Research on iodic acid," *Ann. Chim. Phys.* [5] **13**, 20 (1878); heat of formation.
- 1882THO J. Thomsen, *Thermochemische Untersuchungen* Barth, Leipzig (1882–1886); heat of formation.
- 1896CHR P. Chretien, "Action of sulfuric acid and iodine on iodic acid," *C. R. Acad. Sci.* **123**, 814 (1896); hemihydrate of sulfate.
- 1898CHR P. Chretien, "Study of action that exerts some acids on iodic acid and iodates," *Ann. Chim. Phys.* [7] **15**, 358 (1898); refers to earlier works, formation of hydrates not confirmed later by Moles and Vittorio.
- 1898CHR2 P. Chretien, "Action of sulfuric acid on iodic acid and the iodates," *Ann. Chim. Phys.* **15**, 367 (1898); refers to earlier studies.
- 07BER M. Berthelot, "On the chemical action of radium," *Ann.* **351**, 504 (1907); CA 1 2214(6); decomposition by radium.

- 08GUI M. Guichard, "Action of heat on iodine pentoxide," *Compt. R.* **147**, 1306 (1908); CA 3 1256(1); decomposition, no references.
- 09BEG M. Beger, "On the oxidation of iodine by ozone," *Chem. Ztg.* **33**, 1232 (1909); formation, oxidation of dry iodine with ozone.
- 09FIC/ROH F. Fichter and F. Rohner, "On the oxidation of iodine by ozone," *Berichte* **42**, 4093 (1909); CA 4 879; formation (oxidation of iodine in chloroform with ozone).
- 09GUI M. Guichard, "Action of heat on iodine pentoxide," *Bull. Soc. Chim.* **5**, 86 (1909); CA 3 1256(1); same as C. R. article, decomposition, no references.
- 09GUI2 M. Guichard, "Preparation of pure iodine pentoxide," *C. R.* **148**, 923 (1909); CA 3 1503(5); preparation, same as *Bull. Soc. Chim.* article.
- 09GUI3 M. Guichard, "Preparation of pure iodic anhydride," *Bull. Soc. Chim.* **5**, 722 (1909); CA 3 2544(1); preparation.
- 09MUI M. M. P. Muir, "Iodine dioxide," *J. Chem. Soc.* **95**, 656 (1909); CA 3 1848(9); preparation, IO_2 or I_2O_4 (?), reference to 1844 Millon, reaction with SO_3 .
- 11GUI M. Guichard, "Formation and decomposition of anhydrides," *C. R.* **153**, 1226 (1911); CA 6 721; thermal decomposition.
- 11REI/SCH S. Reich and Schapiro, "Action of iodine pentoxide on acetic anhydride," *Chem. Ztg.* **35**, 409 (1911); CA 6 2910(9); reaction, no initials for Schapiro.
- 12GUI M. Guichard, "Formation and decomposition of anhydrides. Case of iodine pentoxide," *Bull. Chim. Soc.* **11**, 428 (1912); CA 6 3233(9); formation unsuccessful, use existing method, same as C. R. article.
- 12GUI2 M. Guichard, "Combination of iodine and oxygen," *Bull. Soc. Chim.* **11**, 431 (1912); CA 6 3233(9); dissociation review, refers to earlier enthalpy measurements of Berthelot and Thomsen.
- 12KAP H. Kappeler, "Iodine oxides, I_6O_{13} , and $\text{I}_{10}\text{O}_{19}$, and iodine nitrate," *Ber.* **44**, 3496 (1912); CA 6 967(9); existence questioned, said to be $\text{I}_2\text{O}_4(\text{IO} \cdot \text{IO}_3)$, extensive reference to earlier works.
- 15FIC/KAP F. Fichter and H. Kappeler, "Recent observations on iodic salts," *Z. Anorg. Allgem. Chem.* **91**, 134 (1915); CA 9 1587; preparation of $(\text{IO} \cdot \text{IO}_3)$, reference to earlier studies.
- 20LAM/BRA A. B. Lamb, W. C. Bray, and W. J. Geldard, "Preparation of iodic acid and its anhydride," *J. Am. Chem. Soc.* **42**, 1636 (1920); CA 14 2767(7); preparation.
- 22KAT/BLO S. H. Katz and J. J. Bloomfield, "Tests of an iodine pentoxide indicator for carbon monoxide," *J. Ind. Eng. Chem.* **14**, 304 (1922); CA 16 1548(1); CO indicator.
- 23GOM M. Gomberg, "Reaction between silver perchlorate and iodine. Chlorine tetraoxide," *J. Am. Chem. Soc.* **45**, 407 (1923); CA 17 1193; established existence in ether solutions.
- 23LAM/PHI A. B. Lamb and A. W. Phillips, "Solubility of iodine pentoxide in sulfuric acid," *J. Am. Chem. Soc.* **45**, 108 (1923); CA 17 912(7); solubility in H_2SO_4 .
- 29PIR L. R. Pire, "The Ditte reaction," *Anal. Soc. Espan. Fis. Quim.* **27**, 192 (1929); CA 23 3417(1); reaction with CO(g).
- 30BRA W. K. Bray, "An oxide of iodine. An intermediate compound," *J. Am. Chem. Soc.* **52**, 3580 (1930); CA 24 5654(2); proposed I_2O_2 existence as an intermediate.
- 30GRA/FAR F. W. Gray and J. Farquharson, "Diamagnetism and submolecular structure," *Philos. Mag.* [7] **10**, 191 (1930); CA 24 5613(3); structure, diamagnetism.
- 31BAX/BUT G. P. Baxter and A. A. Butler, "The atomic weight of iodine. The analysis of iodine pentoxide," *J. Am. Chem. Soc.* **53**, 968 (1931); CA 25 2066(6); preparation by dehydration of HIO_3 .
- 31CHI Y.-T. Chia, thesis, UCRL-8311 (1931); equilibrium constants.
- 31MOL/PER E. Moles and A. Perez-Vitoria, "Iodine pentoxide and its hydrates," *Z. Phys. Chem. (Bodenstein-Festhandl.)* **583** (1931); CA 26 390(4); preparation by dehydration of HIO_3 , thermal decomposition.
- 31SHA/OZA M. Shah and T. M. Oza, "The interaction between iodine pentoxide and nitric oxide," *J. Chem. Soc.* **32** (1931); CA 25 1753(2); reaction with NO(g).
- 32HUL/BLI O. Hulsmann and W. Blitz, "Molecular and atomic volumes. XLIII. Low temperature densities of crystalline nitric acid, sulfuric acid, phosphorus acid and related substances," *Z. Anorg. Allgem. Chem.* **207**, 377 (1932); CA 26 5800(5); density.
- 32MOL/PER E. Moles and A. Perez-Vitoria, " I_2O_5 and its hydrates, their pyrolysis, densities, heats of solution and hydration," *Anales Soc. Espan. Fis. Quim.* **30**, 99 (1932); CA 26 3161(9); preparation by dehydration of HIO_3 , thermal decomposition, enthalpy of formation, vapor pressure.
- 32MOL/PER2 E. Moles and A. P. Vitoria, "Physicochemical study of the system: $\text{I}_2\text{O}_5\text{-H}_2\text{O}$," *Rev. Acad. Cienc. Madrid* **28**, 573 (1932); CA 26 5821(9); preparation by dehydration of HIO_3 , thermal decomposition of the $\text{H}_2\text{O-I}_2\text{O}_5$ system.
- 33GAR J. Garrido, "The crystalline form of $3\text{I}_2\text{O}_5 \cdot \text{H}_2\text{O}$," *Anal. Soc. Espan. Fis. Quim.* **31**, 616 (1933); CA 28 17(5); crystal form of hydrate.
- 33MOL/PAR E. Moles and A. Parto, "Iodine pentoxide and its hydrates. II," *Anales Soc. Espan. Fis. Quim.* **31**, 618 (1933); CA 28 61(1); hydrate formation, decomposition.
- 34BAX/HAL G. P. Baxter and A. H. Hale, "The atomic weights of iodine, carbon, and sodium. The ratio of iodine pentoxide to sodium carbonate," *J. Am. Chem. Soc.* **56**, 615 (1934); CA 28 2229(1); reaction with Na_2CO_3 .
- 35AST/VAP Astapenya, Vapnik, and Zelkin, "The effect of the surface of the oxidizing agent (iodine pentoxide) on the rate of oxidation of carbon monoxide," *J. Gen. Chem. (USSR)* **3**, 839 (1935); CA 28 2979(8); reaction with CO.
- 35BAH/PAR R. K. Bahl and J. R. Partington, "Lower oxides and sulfates of iodine," *J. Chem. Soc.* **1258** (1935); CA 30 37(4); preparation, thermal decomposition (results differ from those of Muir), refers to earlier studies.
- 36FIC/DIN F. Fichter and A. Dinger, "Iodine sulfate," *Helv. Chim. Acta* **19**, 607 (1936); CA 30 4777(6); formation of sulfate hydrate.
- 36MOL/VIL E. Moles and P. Villan, " I_2O_5 and its hydrates. III," *Anal. Soc. Espan. Fis. Quim.* **34**, 787 (1936); CA 31 6832(4); density.
- 36VIL/MOL P. Villan and E. Moles, "Iodine pentoxide and its hydrates," *Bol. Acad. Cienc. (Madrid)* **2**(8), 5 (1936); CA 30 6513(9); formation of hydrates, dehydration to form I_2O_5 , molecular volume of I_2O_5 .
- 37MAS I. Masson, "Organic and inorganic chemistry of iodine oxides," *Nature* **139**, 150 (1937); CA 31 2540(8); I_2O_3 sulfate.
- 37VAI W. M. Vaidya, "Flame spectra of some aliphatic halides. I. Methyl iodide," *Proc. Indian Acad. Sci.* **6A**, 122 (1937); CA 32 50(8); spectra.
- 38EMS G. Emschwiler, "Photochemical oxidation of methylene iodide: production of iodic anhydride," *C. R.* **206**, 746 (1938); CA 32 3697(6); preparation.

38EMS2	G. Emschwiller, "Production of iodic anhydride by photo-oxidation of organic iodides; photo-oxidation of iodoform and carbon tetraiodide," C. R. 207 , 1201 (1938); CA 33 1597(8); formation.	50EME/WOO	H. J. Emelius and A. A. Woolf, "The reaction of bromine trifluoride with oxides and oxyacid salts," J. Chem. Soc. 164 (1950); CA 44 5750e; reaction with BrF ₃ .
38MAS	J. Masson, "Hypoiodous cations and their action upon an organic reagent," J. Chem. Soc. 1708 (1938); CA 33 1199(4); preparation in solution, I ₂ O proposed as reagent of I ₂ O ₃ sulfate.	50WIL/DHA	W. K. Wilmarth and S. S. Dharmatti, "The magnetic susceptibility of iodine dioxide," J. Am. Chem. Soc. 72 , 5789 (1950); CA 45 3212a; magnetic susceptibility, diamagnetic structure (monomeric IO ₂ does not exist in solid state).
38MAS/ARGO	I. Masson and C. Argument, "Iodous sulfates," J. Chem. Soc. 1702 (1938); CA 33 935(1); preparation of sulfate in solution.	51ADA/SIM	E. G. Adams and N. T. Simmons, "Determination of carbon monoxide by means of iodine pentoxide," J. Applied Chem. (London) 1 , Suppl. 1, S20 (1951); CA 46 4426c; review (preparation, reactivity, stability, 22 references).
38WEB	K. R. Webb, "Solubility of iodine pentoxide in anhydrous hydrogen fluoride and the possible existence of hydrofluorates on iodine pentoxide," Proc. Leeds Philos. Lit. Soc., Sci. Sect. 3, Pt. VIII, 477 (1938); CA 32 7800(5); solubility in HF.	51GYA	B. P. Gyani, "Periodic acid and periodates. II. The system silver oxide-periodic acid-water at 25 °C, J. Phys. Colloid Chem. 55 , 1111 (1951); CA 46 11001d; ternary system Ag ₂ O-I ₂ O ₇ -H ₂ O.
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