Evaluated Chemical Kinetic Data for the Reactions of Atomic Oxygen $O(^3P)$ with Sulfur Containing Compounds

D. L. Singleton

Division of Chemistry, National Research Council of Canada, Ottawa, Canada, K1A 0R9

and

R. J. Cvetanović

Chemical Kinetics Division, Center for Chemical Physics, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Received June 30, 1987; revised manuscript January 19, 1988

Chemical kinetic data for reactions of $O(^3P)$ atoms with sulfur containing compounds are compiled and critically evaluated. Specifically, the reactions considered include the interactions of the ground electronic state of oxygen atoms, $O(^3P)$, with S_2, SF_2, SF_5, SOF, S_2O, SO, SO_2, SO_3, SH, H_2S, D_2S, H_2SO_4, CS, CS_2, COS, CH_3SH, C_2H_5SH, C_3H_7SH, C_4H_9SH, $C_5H_{11}SH$, CH_3SCH_3, cy-CH_2SCH_2, cy-CHCHSCHCH, CH_3SSCH_3, SCF_2, $SCCl_2$, and cy-CF_2SCF_2S. With one exception, the liquid phase reaction $O(^3P)+H_2SO_4 \rightarrow$ products, all the data considered were for gas phase reactions. Where possible, "Recommended" values of the rate parameters have been assessed and conservative uncertainty limits assigned to them.

Key words: Arrhenius parameters; atomic oxygen; chemical kinetics; evaluated kinetic data; $O(^3P)$; rate of reaction; recommended kinetic parameters; sulfur.

Contents

1. Introduction

1.1. Overview

The present evaluation of chemical kinetic data for the elementary reactions of $O(^3P)$ atoms with sulfur containing compounds follows a recent evaluation of kinetic data for the $O(^3P)$ reactions with unsaturated hydrocarbons[1]. As pointed out there, these evaluations represent a part of a larger effort directed towards the development of a comprehensive general evaluated chemical kinetic data base. More specifically, they are a part of the broader data base for all $O(^3P)$ reactions with organic and inorganic reactants. They are thus also a part of an extensive data base, currently developed by the Chemical Kinetics Data Center of the National Bureau of Standards, dealing with chemical oxidation processes, in particular those involved in thermal combustion and in atmospheric chemistry.

The main object of the present evaluation has been to compile as many as possible of the published values of reaction rates of the elementary steps involved in the reactions of $O(^3P)$ atoms with organic and inorganic sulfur containing compounds and to use them to arrive at an estimate of the "recommended" (or "preferred") values of the kinetic parameters and their uncertainties.

1.2. Reaction Mechanisms

There are some far-reaching similarities between the $O(^3P)$ reactions with some of the sulfur containing compounds, especially when sulfur is in a low oxidation state, and those with unsaturated hydrocarbons. As discussed in the earlier evaluation[1], interaction of a ground state oxygen atom, $O(^3P)$, with an organic or inorganic compound may in principle lead to any of the following three types of chemical change: 1) "Abstraction" by the

Reprints available from ACS; see Reprints List at back of issue.

O atom of an atom from the compound, 2) "Addition" of the O atom to the compound, and 3) "Replacement" (or "displacement") by the O atom of an atom or atomic group (radical) from the compound. "Replacement" itself is of necessity initially an addition, combined with subsequent or simultaneous fragmentation of the initial adduct. "Insertion" is a particular type of addition in which the atom inserts into a bond of a compound; for $O(^3P)$ atoms this may be sometimes spin forbidden and not likely to occur (although it is not spin forbidden for $O(^1D_2)$ atoms reacting with hydrocarbons and occurs readily[2]).

Rapid addition of $O(^3P)$ atoms to the CC double bond is the main and perhaps frequently the exclusive initial process in their reactions with alkenes[3-5,6]. Similarly, in the $O(^3P)$ reactions with a number of sulfur containing compounds rapid addition of $O(^3P)$ to an S atom in the compound is the main and perhaps sometimes the exclusive initial process. At least at not too elevated temperature and with $O(^3P)$ atoms not kinetically excited ("hot"), abstraction cannot compete effectively with the very rapid $O(^3P)$ addition to the double bond. However, at sufficiently high temperature, or with sufficiently "hot" $O(^3P)$ atoms, abstraction of H atoms may be expected to become more important[5].

Kinetic behavior of methyl sulfide[7,8] and dimethyl disulfide[8] and of alkenes in their reactions with $O(^3P)$ atoms is very similar: oxygen atoms add very rapidly to S atoms and to CC double bonds, respectively, and, moreover, the activation energies tend to be negative in both cases, especially so in the more rapid of these reactions. In both cases the exothermicities are relatively high and initial adducts tend to undergo rapid fragmentation. In view of these similarities and the type of products formed, it can be assumed that the primary process in the reaction of $O(^3P)$ with methyl sulfide and dimethyl disulfide is $O(^3P)$ attachment to S to form an energy-rich adduct which readily fragments.

The addition mechanism appears to apply also, at least in part, to alkane thiols and probably to some other sulfur organics, as well as to H_2S. However, since the initial adduct rapidly fragments, it is difficult to differentiate, for example, between a primary abstraction and a primary addition. A good example[9] of such mechanistic ambiguity is the reaction $O + H_2S \rightarrow$ products, in which the observed products are OH and SH, i.e. the expected "abstraction" products. In view of such ambiguities, and the considerable analytical difficulties frequently associated with S containing compounds, there remain serious uncertainties in the literature regarding the reaction channels, the branching ratios and finer details of the reaction mechanisms. As a consequence, the primary emphasis in the present evaluation is on the overall rate constants, as it has been also in the earlier evaluation of the related series of $O(^3P)$ reactions with unsaturated hydrocarbons[1]. At the same time, when information is available, alternative reaction channels are indicated in the present evaluation and their rates are listed and the pertinent references given.

1.3. Selection of Recommended Rate Parameters and Their Uncertainty Factors

Reliability of the kinetic data used in the present evaluation has been assessed in particular by scrutinizing the experimental techniques employed, the thoroughness of investigation, the number and precision of measurements, and the consistency with other reported values in the literature when these are available. Although single experimental values have been reported for a number of the reactions considered, some of them are believed to be sufficiently reliable to justify their inclusion into the list of recommended values and assignment of conservatively estimated uncertainty limits. In such cases, as well as when no recommendation is considered possible, or when the derived recommended values are based on more than one reported value but the estimated uncertainty limits are large, further experimental measurements of the rate constants will evidently be needed.

As discussed earlier[1], as a result of potential presence of unknown ("hidden") systematic errors in the measured values of rate constants of a reaction, there are no standard statistical methods for a quantitative evaluation from the data reported in the literature of the expected "best" value and its confidence limits. When two or preferably more values obtained by different techniques have been reported, and there is close agreement between them (within the combined imprecisions), it is reasonable to assume that systematic errors are probably less important than the random errors. In such cases use of standard weighted least squares techniques may be justified and is equivalent to treating any residual systematic errors as random errors.[10] As was done previously[1], in the present evaluation the "recommended values" were generally obtained as the mean weighted least squares values. Depending on the estimated reliability of the data, smaller (and, in rare cases, zero) statistical weights were assigned to some literature values of rate parameters. Thus, for example, for the O atom reaction with dimethyl sulfide at 300 K, the k value of 74 CAD/WIC is two orders of magnitude smaller than the other values for the same reaction and is therefore assigned zero weight.

Since the procedure used is of necessity subjective, conservatively estimated probable overall uncertainties were assigned to the selected "recommended" values of k and the Arrhenius A factor. It was found convenient to express these uncertainties in k and A in the form of uncertainty factors (which must not be taken to imply that the errors in the rate constants are necessarily lognormally distributed). The uncertainties assigned to the Arrhenius B, expressed as additive ($\pm$) deviations, are also approximate estimates.

The evaluation covers the investigated (and documented in the literature) $O(^3P)$ reactions with organic and inorganic sulfur containing compounds. With one exception, only gas phase reactions have been considered. For previous evaluations of kinetic data for some of these reaction systems see, for example, Reference 11.

1.4. Organization

The material presented in this article is divided into four sections. Section 1 is the Introduction. Section 2 gives a brief summary of the adopted symbols and units. Section 3 contains a table of all recommended kinetic parameters and the page numbers indicating the locations of the detailed tabulations of the kinetic data for the listed reactions. Section 4 contains the data sheets for $O(^3P)$ reactions with organic and inorganic sulfur containing compounds with the lists of references.

1.5. Guide to Summary of Recommended Rate Parameters

The Table in Section 3 summarizes the recommended values of the kinetic parameters for the listed gas phase second and third order reactions. The information is displayed in 7 columns. Column 1 ("Reaction") contains the reaction formula and the chemical name of the species reacting with $O(^3P)$ atoms. If Column 2 ("T/K") contains a single temperature, e.g. 298, the value in Column 3 ("k,A") is k at that temperature; if it contains a temperature range, e.g. 200–500, the value in Column 3 is the Arrhenius A. The units of k and A for the second and third order reactions are $cm^3\ mol^{-1}\ s^{-1}$ and $cm^6\ mol^{-2}\ s^{-1}$, respectively. The values are given in exponential form, written as (1.00±0.10)(11), which signifies $(1.00\pm0.10)\times10^{11}$.

Columns 4 ("n") and 5 ("B") contain, if applicable, the n and B parameters in the extended Arrhenius Eq. $k=A(T/298)^n\exp(-B/T)$. Column 6 ("k err. factor") contains the assigned uncertainty factors of k and A, and Column 7 ("Page") lists the page number showing the location of the detailed tabulation of kinetic data for the reaction.

1.6. Guide to the Reaction Data Sheets

With one exception, all kinetic data listed are for gas phase reactions. The data in the Data Sheets are divided into eight columns. Column 1 ("Reference Code, Notes") contains Reference Code and Notes relevant to the data entered and the techniques employed. When, for brevity, the reference code is omitted from Column 1 of a data line, it is the same as the closest reference code in Column 1 in one of the preceding data lines. The Reference Code consists of the last two digits of the year of publication, followed by the first three letters of the names of the first and second author (if present) separated by a slash. An integer index is attached at the end when it is necessary to differentiate between otherwise identical Codes. This is illustrated by the Code 80 LEE/TAN2. Column 2 ("Data type") contains the two-character Data Type Codes listed in Section 2. If Column 3 ("T/K") contains a single temperature, e.g. 298, the value in Column 4 ("k, k/k(ref), A, A/A(ref)") is k (or k/k(ref)) at that temperature; if it contains a temperature range, e.g. 200–500, the value in Column 4 is the Arrhenius A parameter (or A/A(ref)). Column 5 ("n") and Column 6 ("B,$B-B$(ref)"), respectively, contain, when applicable, the n and B (or $B-B$(ref)) parameters in the extended Arrhenius Eq. $k=A(T/298)^n\exp(-B/T)$. k(ref), A(ref) and B(ref) are the kinetic parameters of the reference reaction in relative rate determinations. Column 7 ("k,A units") specifies the reaction order and thus defines the units of k and A, as listed in Section 2. Column 8 ("k err. factor") lists the overall uncertainty factors assigned to k and A.

1.7. Acknowledgments

This work was supported by the Department of Energy, Division of Basic Energy Sciences and the Office of Standard Reference Data, National Bureau of Standards.

1.8. References to the Introduction

[1] Cvetanović, R. J., "Evaluated Chemical Kinetic Data for the Reactions of Atomic Oxygen $O(^3P)$ with Unsaturated Hydrocarbons," J. Phys. Chem. Ref. Data **16**, 261 (1987).

[2] Yamazaki, H., and Cvetanović, R. J., "Collisional Deactivation of the Excited Singlet Oxygen Atoms and Their Insertion into the CH Bonds of Propane," J. Chem. Phys. **41**, 3703 (1964).

[3] Cvetanović, R. J., "Electrophilic Character of Oxygen Atoms," Can. J. Chem. **38**, 1678 (1960).

[4] Cvetanović, R. J., "Addition of Atoms to Olefins in the Gas Phase," Adv. Photochem. **1**, 115 (1963).

[5] Cvetanović, R. J., and Singleton, D. L., "Reaction of Oxygen Atoms with Olefins," Rev. Chem. Inter. **5**, 183 (1984).

[6] Huie, R. E., and Herron, J. T., "Reactions of Atomic Oxygen (O^3P) with Organic Compounds," Prog. React. Kinet. **8**, 1 (1975).

[7] Slagle, I. R., Graham, D. E., and Gutman, D., "Direct Identification of Reactive Routes and Measurement of Rate Constants in the Reactions of Oxygen Atoms with Methanethiol, Ethanethiol, and Methylsulfide," Int. J. Chem. Kinet. **8**, 451 (1978).

[8] Cvetanović, R. J., Singleton, D. L., and Irwin, R. S., "Gas-Phase Reactions of $O(^3P)$ Atoms with Methanethiol, Ethanethiol, Methyl Sulfide, and Dimethyl Disulfide. 2. Reaction Products and Mechanisms," J. Am. Chem. Soc. **103**, 3530 (1981).

[9] Singleton, D. L., Paraskevopoulos, G., and Irwin, R. S., "Mechanism of the $O(^3P)$ + H_2S Reaction. Abstraction or Addition?," J. Phys. Chem. **86**, 2605 (1982).

[10] Cvetanović, R. J., Singleton, D. L., and Paraskevopoulos, G., "Evaluations of the Mean Values and Standard Errors of Rate Constants and Their Temperature Coefficients," J. Phys. Chem. **83**, 50 (1979).

[11] Herron, J. T., and Huie, R. E., "Rate Constants for the Reactions of Atomic Oxygen (O^3P) with Organic Compounds in the Gas Phase," J. Phys. Chem. Ref. Data **2**, 467 (1973).

2. Summary of Symbols and Units

Reaction Phase Codes:

G=gas, L=liquid, S=solid, M=mixed phases (gas-liquid, gas-solid, liquid-solid, gas-liquid-solid)

Data Type Codes:

EX (experimentally measured absolute value),
RL (experimentally measured relative value),
RN (RL normalized to absolute value),
TH (theoretical value),

DE (derived indirectly, e.g. using reverse rate and equilibrium constant, or computer simulation of a complex mechanism)
CO (computed numerically),
ES (estimated, by analogy etc.),
SE (selected in the literature as probable "best" value),
RE (currently recommended value).

Type of excitation:
(EXV) (vibrationally excited)
(EXT) (translationally excited)
(EXE) (electronically excited)
(EXEV) (electronically and vibrationally excited), etc.

Decadic exponent notation:
1.2(11) (stands for 1.2×10^{11})

Temperature (T): in kelvins (K).

Arrhenius parameters are defined by
$k = A(T/298)^n \exp(-B/T)$

Unit Codes for k, k/k(ref), A, A/A(ref):
1 (s^{-1})
2 ($cm^3\ mol^{-1}\ s^{-1}$)
3 ($cm^6\ mol^{-2}\ s^{-1}$)
1/1, 2/2 etc. (dimensionless)
2/1 ($cm^3\ mol^{-1}$), etc.

($T/298$) and n (the exponent of T) are dimensionless.

Units for B, $B - B$(ref): kelvins (K). (Arrhenius parameter $E = R \times B$).

k(ref), A(ref) and B(ref) are the values for the "reference reaction" in relative rate determinations.

k err. factor: Estimated overall Uncertainty Factor. It multiplies and divides k or A to indicate approximate error limits. It does not imply that errors in k are necessarily lognormally distributed.

3. Index of Reactions and Summary of Recommended Rate Parameters

Reaction		T/K	k,A $\mathrm{cm^3mol^{-1}s^{-1}}$	n	B	k err. factor	Page
O + S_2 → products		409	7(12)			1.2	1384
O + Sulfur dimer		298	1(13)			4	
(Tentative suggestion for 298K)							
O + SF_2 → products		298	6.5(13)			1.3	1385
O + Sulfur fluoride (SF_2)							
O + SF_5 → products		298	1.2(13)			1.3	1385
O + Sulfur fluoride (SF_5)							
O + SOF → products		298	4.8(13)			2	1386
O + Sulfur fluoride oxide							
O + S_2O → products		298	9.3(11)			1.3	1386
O + Sulfur oxide (S_2O)							
O + SO + M → SO_2 + M	(k_∞)	298	3.2(13)			1.5	1387
O + Sulfur monoxide	(M=Ar)	298	1.85(17)$\mathrm{cm^6mol^{-2}s^{-1}}$			1.2	
k relative to k(M=Ar) at 298K:							
Ar=1.0, Ne=0.88, Kr=1.18, He=1.25,							
Xe=1.28, N_2=1.51, CF_4=7.84,							
CO_2=8.22, CH_4=8.65, SF_6=9.62,							
C_3F_8=12.2, H_2=13.7, D_2=13.7.							
O + SO → SO_2 + hν		298	2(8)			3	1389
O + Sulfur monoxide							
O + SO_2 + M → SO_3 + M	(M=Ar)	299	3.7(14)$\mathrm{cm^6mol^{-2}s^{-1}}$			1.3	1390
O + Sulfur dioxide	(M=Ar)	299-440	1.1(16)$\mathrm{cm^6mol^{-2}s^{-1}}$		1010±200	1.5	
	(M=Ar)	1700-2500	1.06(13)$\mathrm{cm^6mol^{-2}s^{-1}}$		-7870	2	
	(M=He)	298	3.5(14)$\mathrm{cm^6mol^{-2}s^{-1}}$			1.3	
	(M=He)	248-415	4.0(16)$\mathrm{cm^6mol^{-2}s^{-1}}$		1400±200	1.5	
k relative to k(M=Ar) at 298K:							
Ar=1.0, He=0.9, N_2=1.3, O_2=1.3.							
N_2O=3, SO_2=10, within about 30%,							
for SO_2 up to a factor of 3.							
O + SO_2 → SO + O_2		440-3000	5(12)		9800	3	1396
O + Sulfur dioxide							
O + SO_3 → products							1397
O + Sulfur trioxide							

Index of Reactions and Summary of Recommended Rate Parameters -- Continued

Reaction	T/K	k,A $cm^3mol^{-1}s^{-1}$	n	B	k err. factor	Page
$O + SO_3 + M \rightarrow SO_2 + O_2 + M$						1399
O + Sulfur trioxide						
$O + SH \rightarrow H + SO$	298	1.4(14)			3	1400
O + Mercapto						
$O + SH \rightarrow OH + S$						1401
O + Mercapto						
$O + H_2S \rightarrow$ products	298	1.5(10)			1.3	1401
O + Hydrogen sulfide	263-502	6.0(12)		1789±200	1.8	
$O + D_2S \rightarrow OD + SD$	298	4.7(9)			1.4	1405
O + Deuterium sulfide	298-450	6.3(12)		2144±200	2	
$O + H_2S \rightarrow SO + H_2$						1405
O + Hydrogen sulfide						
$O + H_2S \rightarrow HSO + H$	298	<0.2 *)			1.1	1406
O + Hydrogen sulfide						
*) Branching ratio (nondimensional)						
$O + H_2SO_4 \rightarrow$ products	298	#)				1407
O + Sulfuric acid						
#) Rn. probability per collison < 1.0(-6) (nondimensional).						
$O + CS \rightarrow$ products	298	1.2(13)			1.2	1408
O + Carbon monosulfide	156-305	1.5(14)		751±100	1.5	
$O + CS_2 \rightarrow$ products	298	2.3(12)			1.2	1411
O + Carbon disulfide	218-920	3.55(13)		821±100	1.5	
$O + CS_2 \rightarrow COS + S$	298	2.1(11)			1.3	1415
O + Carbon disulfide	249-500	2.2(12)		701±100	2	
$O + CS_2 \rightarrow CO + S_2$	298	1.4(-2) *)			1.2	1416
O + Carbon disulfide k(298K)	298	3.5(10)			1.3	
*) Branching ratio (nondimensional)						
$O + COS \rightarrow$ products	298	8.0(9)			1.2	1417
O + Carbon oxide sulfide	239-523	1.6(13)		2257±200	1.3	
	239-1900	4.7(13)		2621±200	1.5	
$O + COS \rightarrow CO_2 + S$	1200	5(11)			3	1422
O + Carbon oxide sulfide	1200-1900	5(13)		5530±1000	3	

Index of Reactions and Summary of Recommended Rate Parameters -- Continued

Reaction	T/K	k,A $cm^3mol^{-1}s^{-1}$	n	B	k err. factor	Page
O + CH_3SH → products	298	1.2(12)			1.2	1422
O + Methanethiol	252-661	*)	*)	*)	1.3	
*) Strongly curved Arrhenius plot: k=A1+A2exp(-B/T) with A1=9.0(11), A2=1.8(13), B=1261.						
O + C_2H_5SH → products	298	1.7(12)			1.2	1424
O + Ethanethiol	256-574	*)	*)	*)	1.4	
*) Strongly curved Arrhenius plot: k=A1+A2exp(-B/T) with A1=1.6(12), A2=1.0(14), B=2198.						
O + C_3H_7SH → products	298	1.6(12)			1.3	1427
O + 1-Propanethiol	303-421	8.3(12)		494±50	1.5	
O + C_4H_9SH → products	298	2.0(12)			1.3	1427
O + 1-Butanethiol	306-419	5.8(12)		321±50	1.5	
O + $C_5H_{11}SH$ → products	298	2.1(12)			1.3	1428
O + 1-Pentanethiol	302-409	6.2(12)		328±50	1.5	
O + CH_3SCH_3 → products	298	3.1(13)			1.2	1429
O + Methane, thiobis-	252-557	8.2(12)		-397±100	1.3	
O + cy-CH_2SCH_2 → products	298	7.6(12)			1.3	1431
O + Ethylene episulfide	268-424	8.1(12)		18±50	1.5	
O + cy-CHCHSCHCH → products						1432
O + CH_3SSCH_3 → products	298	6.0(13)			1.2	1433
O + Disulfide, dimethyl-	298-570	2.6(13)		-250±100	1.5	
O + SCF_2 → products	298	2.1(12)			1.5	1435
O + Carbonothioic difluoride	259-493	7.4(12)		376±100	1.5	
O + $SCCl_2$ → products	298	2.3(13)			1.3	1436
O + Carbonothioic dichloride	251-493	1.9(13)		-60±100	1.5	
O + cy-CF_2SCF_2S → products	298	8.1(11)			1.3	1437
O + 1,3-dithietane, 2,2,4,4-tetrafluoro-	253-493	1.4(13)		855±100	1.5	

4. Reaction Data Sheets

O + S_2 → products

O + Sulfur dimer

The assumed reaction product is SO+S (68 HOM/KRO, 87 HIL/CIC).

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
68 HOM/KRO Discharge flow. O formed by microwave discharge in N_2/Ar, followed by N+NO→O+N_2. SO formation monitored by mass spec. Excess [S_2] over [O]. P=2 Torr. Uncertainty is an order of magnitude.	EX	1050	4(12)			2	
73 SCH Only one reported value (68 HOM/KRO).	SE	1050	4(12)			2	
87 HIL/CIC	EX	409	(6.62±0.78)(12)			2	
Discharge flow. Decay of S_2 in excess O monitored by mass spec. O formed by microwave discharge in O_2. For absolute k measurement, [O] was determined by titration with excess NO_2. For relative rate measurement, O + NO_2 was used as the reference rn. (taking k_{ref}=5.6(12) from 85 DEM/MAR). Decay of NO_2 was measured in excess O. P = 0.89-1.60 Torr.	RN	409	(7.17±1.02)(12)			2	
Recommended value of k	RE	409	7(12)			2	1.2
Suggested tentative value of k at 298 K	RE	298	1(13)			2	4
Based on the data of 87 HIL/CIC and potential extreme values of 68 HOM/KRO. More determinations are needed.							

References for reaction O + S_2 → products

68 HOM/KRO	Homann, K.H., Krome, G., and Wagner, H.Gg., "Schwefelkohlenstoff-oxydation, geschwindigkeit von elementarreaktionen. Teil 1," Ber. Bunsenges. Phys. Chem. 72, 998 (1968).
73 SCH	Schofield, K., "Evaluated chemical kinetic rate constants for various gas phase reactions," J. Phys. Chem. Ref. Data 2, 25 (1973).
85 DEM/MAR	NASA Panel for Data Evaluation: DeMore, W.B., Margitan, J.J., Molina, M.J., Watson, R.T., Golden, D.M., Hampson, R.F., Kurylo, M.J., Howard, C.J., and Ravishankara, A.R., "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling. Evaluation number 7," J.P.L. Publ. 85-37 (1985).
87 HIL/CIC	Hills, A.J., Cicerone, R.J., Calvert, J.G., and Birks J.W., "Kinetics of the reactions of S_2 with O, O_2, O_3, N_2O, NO, and NO_2," J. Phys. Chem., 91, 1199 (1987).

O + SF_2 → products

O + Sulfur fluoride (SF_2)

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
86 PLU/RYA Discharge flow-mass spec. Decay rate of SF_2 in excess O. O and SF_2 formed by microwave discharge in O_2/He and in SF_6/He. SOF, SO, and SO_2 were detected as products.	EX	295	(6.5±1.2)(13)			2	
Recommended value of k Based on the only data available (86 PLU/RYA). Additional determinations would be useful.	RE	298	6.5(13)			2	1.3

Reference for reaction O + SF_2 → products

86 PLU/RYA Plumb I.C., and Ryan K.R., "Gas-phase reactions of SF_5, SF_2, and SOF with $O(^3P)$: their significance in plasma processing," Plasma Chem. Plasma Processing, 6, 247-258 (1986).

O + SF_5 → products

O + Sulfur fluoride (SF_5)

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
86 PLU/RYA Discharge flow-mass spec. Decay rate of SF_5 in excess O. O and SF_5 formed by microwave discharge in O_2/He and in SF_6/He. Products are assumed to be SOF_4+F.	EX	295	(1.2±0.3)(13)			2	
Recommended value of k Based on the only data available (86 PLU/RYA). Additional determinations would be useful.	RE	298	1.2(13)			2	1.3

Reference for reaction O + SF_5 → products

86 PLU/RYA Plumb I.C., and Ryan K.R., "Gas-phase reactions of SF_5, SF_2, and SOF with $O(^3P)$: their significance in plasma processing," Plasma Chem. Plasma Processing, 6, 247-258 (1986).

O + SOF → products

O + Sulfur fluoride oxide

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
86 PLU/RYA	EX	295	(4.8±1.2)(13)			2	
Discharge flow-mass spec. Analysis of the formation and decay of SOF in the rn. O+SF_2. O and SF_2 formed by microwave discharge in O_2/He and in SF_6/He.							
Recommended value of k	RE	298	4.8(13)			2	2
Based on the only data available (86 PLU/RYA). Additional determinations would be useful.							

Reference for reaction O + SOF → products

86 PLU/RYA Plumb I.C., and Ryan K.R., "Gas-phase reactions of SF_5, SF_2, and SOF with O(^{3}P): their significance in plasma processing," Plasma Chem. Plasma Processing, 6, 247-258 (1986).

O + S_2O → products

O + Sulfur oxide (S_2O)

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
74 STE/ALV	RL	298	0.17±0.02			2/2	
	RN	298	(9.3±1.2)(11)			2	
Reference rn. is O+NO_2→NO+O_2. Discharge flow. O formed by microwave discharge of O_2/Ar or by N+NO rn. The RL value obtained by comparing the O+SO and O+NO chemiluminescences for different flow rates of S_2O and NO_2. [RN value has been updated using k_{ref}=5.6(12) (85 DEM/MAR)]. SO observed as a product.							
Recommended value of k	RE	298	9.3(11)			2	1.3
Based on the only data available (74 STE/ALV). Additional determinations would be useful.							

References for reaction O + S_2O → products

74 STE/ALV Stedman, D.H., Alvord, H., and Baker-Blocker, A., "Chemiluminescent reactions of disulfur monoxide," J. Phys. Chem. 78, 1248 (1974).

References for reaction O + S_2O → products -- Continued

85 DEM/MAR NASA Panel for Data Evaluation: DeMore, W.B., Margitan, J.J., Molina, M.J., Watson, R.T., Golden, D.M., Hampson, R.F., Kurylo, M.J., Howard, C.J., and Ravishankara, A.R., "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling. Evaluation number 7," J.P.L. Publ. 85-37 (1985).

O + SO + M → SO_2 + M

O + Sulfur monoxide

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
66 HAL/THR Discharge flow. O and SO formed by microwave discharge in SO_2/Ar. [O] and [SO] monitored by O+NO and O+SO chemiluminescences.	EX	300	(3.2±0.4)(17)			3	
67 SHA/PAD *) Room T. M=Ar. P=0.8 Torr. Obtained SO in the rn. O+COS. Rate of light emission measured relative to the reaction O+NO→NO_2+hv. The second order rate constant was derived using k(O+NO→NO_2+hv), k(O+COS→CO+SO), and relative emission intensities of the O+NO→NO_2+hv and O+SO→SO_2+hv rns. The listed termolecular k was obtained by dividing the second order constant by P. (See also 67 SHA/PAD in the next data sheet).	RN	*)	8.0(16)			3	
70 TAK M=Ar. P(Ar)=4.2 Torr. Discharge flow. O formed by microwave discharge of N_2O/Ar. [O] monitored by chemiluminescence from O+NO_2 and O+NO Rns. SO formed by reaction of excess O with H_2S, and its decay monitored by chemiluminescence from O+SO reaction.	EX	293	5.8(16)			3	
71 MIY/TAK *) Room temperature. M=Ar. P=3.8 Torr. Discharge flow. O formed by microwave discharge of N_2O/Ar. SO formed by reaction of O with CS_2. Formation of SO_2 monitored by its chemiluminescence. k calculated from the integrated rate equation for initially equal [O] and [SO].	EX	*)	7.3(16)			3	
73 SCH Based on only one measurement (66 HAL/THR).	SE	300	3.2(17)			3	

O + SO + M → SO_2 + M -- Continued

Reference Code, Notes		Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
76 BAU/DRY		SE	298	(6.7±2.0)(16)			3	
M=Ar.								
78 HAM/GAR		SE	298	6.7(16)			3	1.3
M=Ar. Accepted recommendation of 76 BAU/DRY.								
85 COB/HIP	(M=Ar P=0.2-200 bar)	EX	300	1.85(17)			3	
	(M=N_2 P=0.2-200 bar)	EX	300	2.79(17)			3	
	(M=C_3F_8 P=0.2-3 bar)	EX	300	2.25(18)			3	
	(M=He P=0.2-25 bar)	EX	300	2.32(17)			3	
	(M=Ne P=0.5-5 bar)	EX	300	1.63(17)			3	
	(M=Kr P=1-5 bar)	EX	300	2.18(17)			3	
	(M=Xe P=0.2-5 bar)	EX	300	2.36(17)			3	
	(M=H_2 P=0.5-5 bar)	EX	300	2.54(18)			3	
	(M=D_2 P=0.5-5 bar)	EX	300	2.54(18)			3	
	(M=CO_2 P=0.2-5 bar)	EX	300	1.52(18)			3	
	(M=CH_4 P=0.5-5 bar)	EX	300	1.60(18)			3	
	(M=CF_4 P=0.2-5 bar)	EX	300	1.45(18)			3	
	(M=SF_6 P=0.2-5 bar)	EX	300	1.78(18)			3	
	(k∞, high P limit)	EX	300	3.2(13)			2	
O and SO formed by laser photolysis of SO_2 at 193nm. k values obtained from 2nd order plots of uv absorption, used to monitor SO_2 reformation. Pressure of third body ranged from 0.2 to 200 bar. k∞ (high pressure limit) is based on data for M=Ar, N_2, and C_3F_8. Used broadening factors (Fc) of 0.55, 0.58 and 0.76 to fit the data for N_2, Ar and C_3F_8, respectively.								
Recommended value of k∞ (high P limit)		RE	298	3.2(13)			2	1.5
Recommended value of k(M=Ar)		RE	298	1.85(17)			3	1.2

Recommended third body efficiencies at 298 K (i.e. k values relative to k(M=Ar)): Ar=1.00, Ne=0.88, Kr=1.18, He=1.25, Xe=1.28, N_2=1.51, CF_4=7.84, CO_2=8.22, CH_4=8.65, SF_6=9.62, C_3F_8=12.2, H_2=D_2=13.7. The recommended values are based on the extensive data of 85 COB/HIP. (The average of the listed k(M=Ar) values, excluding the value of 67 SHA/PAD, which is apparently for the rate of the third order light emission, is only 16% smaller than the recommended value of 1.85(17)).

References for reaction O + SO + M → SO_2 + M

66 HAL/THR Halstead, C.J. and Thrush, B.A., "The kinetics of elementary reactions involving the oxides of sulphur. II. Chemical reactions in the sulphur dioxide afterglow," Proc. Roy. Soc. A **295**, 363 (1966).

67 SHA/PAD Sharma, A., Padur, J.P., and Warneck, P., "The chemiluminescent reactions of atomic oxygen with carbonyl sulfide and hydrogen sulfide," J. Phys. Chem. 71, 1602 (1967).

References for reaction $O + SO + M \rightarrow SO_2 + M$ -- Continued

70 TAK	Takahashi, S., "The study of the reaction of hydrogen sulphide with atomic oxygen using emission spectrum," Mem. Nat. Def. Acad. Japan **10**, 369 (1970).
71 MIY/TAK	Miyazaki, S., and Takahashi, S., "On the reaction of oxygen atom with carbon disulfide (Part 2)," Mem. Nat. Def. Acad. Japan **11**, 307 (1971), C.A. **78**, 62771w (1973).
73 SCH	Schofield, K., "Evaluated chemical kinetic rate constants for various gas phase reactions," J. Phys. Chem. Ref. Data **2**, 25 (1973).
76 BAU/DRY	Baulch, D.L., Drysdale, D.D., Duxbury, J., and Grant, S.J., "Homogeneous gas phase reactions of the O_2-O_3 system, the CO-O_2-H_2 system, and of sulphur-containing species," in 'Evaluated Kinetic Data for High Temperature Reactions', Vol. **3**, Butterworths, London (1976).
78 HAM/GAR	Hampson, R.F., Jr., and Garvin, D., editors, "Reaction rate and photochemical data for atmospheric chemistry - 1977," Nat. Bur. Stand. Spec. Publ. **513** (1978).
85 COB/HIP	Cobos, C.J., Hippler, H., and Troe J., "Falloff curves of the recombination reaction $O + SO + M \rightarrow SO_2 + M$ in a variety of bath gases," J. Phys. Chem. **89**, 1778 (1985).

$O + SO \rightarrow SO_2 + h\nu$

O + Sulfur monoxide

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
65 ROL/REE *) Room temperature. P < 0.02 Torr. Rate constant for light emission. Discharge flow. Excess O, formed by discharge in O_2. SO obtained from O+COS rn. Rate constant determined relative to light emission from O+NO.	RN	*)	4.2(8)			2	
66 HAL/THR Rate constant for light emission. Discharge flow. Excess O, formed by discharge in O_2/Ar. SO obtained from O+COS rn. k determined relative to light emission from O+NO. Intensity was independent of Ar pressure, at P=0.2-1.6 Torr.	RN	298	1.5(8)			2	
67 SHA/PAD *) Room T. Discharge flow in O_2 or O_2/Ar. O+COS gives SO. Measured light emission at 0.8 Torr relative to $O+NO \rightarrow NO_2+h\nu$. Listed k derived using $k(O+NO \rightarrow NO_2+h\nu)$, $k(O+COS \rightarrow CO+SO)$, and relative emission intensities of $O+NO \rightarrow NO_2+h\nu$ and $O+SO \rightarrow SO_2+h\nu$ rns. Measured light emission is assumed to be sum of contributions from a small second order and a larger third order process. (See also 67 SHA/PAD in the preceding data sheet).	RN	*)	3.4(9)			2	

$O + SO \rightarrow SO_2 + h\nu$ -- Continued

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
69 FLE/LEV Shock tube study of SO_2/Ar mixtures. Calibrated the optical system with tungsten and hydrogen lamps. [O] and [SO] calculated assuming equilibrium for the species SO_2, Ar, SO, O, O_2, and SO_3. Adopting k=1.5(8) at 298 K (66 HAL/THR), the authors calculate A=1.5(8), n=-1.0, B=0. Total P ~ 0.5 atm.	EX	3500	(1.4±0.4)(7)			2	
Recommended value of k Additional experimental work is desirable.	RE	298	2(8)			2	3

References for reaction $O + SO \rightarrow SO_2 + h\nu$

65 ROL/REE Rolfes, T.R., Reeves, R.R., Jr., and Harteck, P., "The chemiluminescent reaction of oxygen atoms with sulfur monoxide at low pressures," J. Phys. Chem. 69, 849 (1965).

66 HAL/THR Halstead, C.J. and Thrush, B.A., "The kinetics of elementary reactions involving the oxides of sulphur. II. Chemical reactions in the sulphur dioxide afterglow," Proc. Roy. Soc. A **295**, 363 (1966).

67 SHA/PAD Sharma, A., Padur, J.P., and Warneck, P., "The chemiluminescent reactions of atomic oxygen with carbonyl sulfide and hydrogen sulfide," J. Phys. Chem. 71, 1602 (1967).

69 FLE/LEV Fletcher, S.R., and Levitt, B.P., "O + SO recombination emission at 3500K," Trans. Faraday Soc. 65, 1544 (1969).

$O + SO_2 + M \rightarrow SO_3 + M$

O + Sulfur dioxide

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
58 KAU *) Room temperature. M=O_2. Discharge flow. O formed by microwave discharge in O_2. Decay of O in excess SO_2 determined from intensity of the O+NO chemiluminescence. Detailed experimental conditions not reported.	EX	*)	3(16)			3	

$O + SO_2 + M \rightarrow SO_3 + M$ -- Continued

Reference Code, Notes		Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
65 LEV/MER Microprobe study of $H_2S/O_2/N_2$ or of $H_2S/O_2/Ar$ flames. Mass spec. analyses for O_2, H_2S, H_2O, H_2, and SO_2; wet analyses for $SO + SO_2$ and SO_3. Calculated equilibrium concentrations of atoms and radicals. k's derived from observed $[SO_2]$ and $[SO_3]$ profiles. The value for B is assumed.		DE	300-1300	(2.2-22)(15)		3019	3	
65 WEB/WAL $M=H_2+O_2$. P=27.9 Torr. Reference rn. $O+H_2 \rightarrow OH+H$ (used k=2.0(10)). Determined second explosion limits for H_2/O_2 mixtures with and without SO_2.		RN	784	1.1(16)			3	
66 CAD/POW $M=N_2$. Discharge flow. O from microwave discharge in O_2 or in N_2 followed by $N+NO \rightarrow O+N_2$. k determined from initial decrease in [O] (measured by O+NO luminescence) and $[SO_2]$ decrease (measured by gas chromatography). Activation energy reported as near 0. N_2 and O_2 are equally efficient as third bodies.		EX	300	4.7(15)			3	
66 HAL/THR M=Ar. Discharge flow. O formed by microwave discharge in O_2/Ar mixture. Monitored O in excess SO_2 by O+NO chemiluminescence. The efficiency of Ar relative to O_2 is 1.0±0.2. Pressure range is not reported.		EX	293	(4.7±0.8)(15)			3	
66 JAF/KLE $M = SO_2$. Photolysis of NO_2 in presence of SO_2. k derived from quantum yield of NO_2 consumption, ^{18}O isotope exchange, and rate constant for the $O+NO_2$ rn. The k value is for P=2 Torr.		DE	297	1.4(16)			3	
67 MUL/STE	($M=SO_2$ P=0.7-3 Torr)	EX	299	(1.0±0.4)(16)			3	
	(M=Ar P=0.7-3 Torr)	EX	299	(2.4±0.15)(15)			3	
	($M=O_2$ P=0.7-3 Torr)	EX	299	(2.7±0.5)(15)			3	
Stirred flow - ESR detection of O. Excess SO_2. Allowance not made for influence of SO_3 on the wall recombination of O atoms (see 69 MUL/STE).								

$O + SO_2 + M \rightarrow SO_3 + M$ -- Continued

Reference Code, Notes		Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
69 MUL/STE Supercedes 67 MUL/STE for M=Ar. P(Ar)=2-6 Torr. Stirred flow. O formed by microwave discharge in O_2 in excess Ar and monitored by O+NO chemiluminescence and ESR. Allowance made for influence of SO_3 on the wall recombination of O.		EX	300	(1.1±0.3)(15)			3	
69 NET/STI M=N_2. Sampled with an alumina tube the flames composed of either CH_4 or CO with O_2, SO_2, and N_2. Determined CO, CO_2, O_2, SO_3, and SO_2. Rate constant is based on the SO_3 production, the calculated equilibrium concentrations of O, and the value k=1(12) for $O+SO_3 \rightarrow SO_2+O_2$ rn. The authors suggest that the value of k is a lower limit.		DE	2150	≥2(15)			3	
71 HEI/WOO *) Room temperature. M=N_2O. O formed by Hg-photosensitized decomposition of N_2O in the presence of COS. SO_2 produced in secondary reactions. Rate constant determined relative to O+COS, based on yields of N_2 and CO. The authors indicate a large experimental uncertainty.		RL	*)	5(6)			3/2	
71 TIM/LEF	(M=SO_2)	EX	298	4.10(16)			3	
	(M=Ar)	EX	298	1.0(15)			3	
	(M=He)	EX	298	8(14)			3	
Discharge flow-ESR detection of O. Excess SO_2. Allowance is made for the third body effect of SO_2. An Arrhenius plot is given for M=SO_2 at 205K<T<298K (values of A and B are not quoted).								
73 SCH M=Ar. Estimated a factor of 2 error at 300 K, greater at other temperatures. Third body efficiencies taken to be about the same for Ar, O_2, N_2, He, and from 6 to 40 times greater for SO_2, NO_2, N_2O.		SE	250-1000	3.6(14)		-503	3	

$O + SO_2 + M \rightarrow SO_3 + M$ -- Continued

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
74 ATK/PIT M=N_2O. P(N_2O)=54-135 Torr. Phase shift technique. O atoms generated by the Hg-photosensitized decomposition of N_2O. O monitored by the O+NO chemiluminescence. An upper limit of k(SO_2)/k(N_2O) = 5 assessed for SO_2 and N_2O as third bodies (see also 78 ATK/PIT).	EX	299-392	3.32(16)		1006±200	3	
74 DAV M=N_2. Flash photolysis-resonance fluorescence. Relative third body efficiencies N_2:He:Ar:SO_2= 1.0:0.45:0.87:60. Few details. Reference to unpublished data of D.D. Davis, R. Schiff, and S. Fischer.	EX	220-353	1.2(16)		1120	3	
75 WES/DEH2 (M=He P=0.7-6.7 Torr)	EX	248-415	(3.9±0.9)(16)		1400±50	3	
(M=N_2 P=0.7-6.7 Torr)	EX	297	(7.2±0.3)(14)			3	
(M=SO_2 k_{rel}=k/k(M=He)) Discharge flow-ESR detection of O. Excess SO_2. Allowance is made for the third body effect of SO_2.	RL	297	9.5±2.7			3/3	
76 BAU/DRY *) No new recommendation. Suggest using Davis's data (see entry for 74 DAV).	SE		*)			3	
78 ATK/PIT M=Ar. P(Ar)=25-50 Torr. Flash photolysis - NO_2 chemiluminescence. O formed by photolysing SO_2 and NO. [O] was followed by the O+NO chemiluminescence. The effect of SO_2 as third body was taken into account. Relative k values for different M at 300 K are Ar:N_2:N_2O:SO_2 = 1.0:1.3:3.0:9.0.	EX	299-440	1.12(16)		1009±151	3	
78 HAM/GAR M=N_2. Relative k values for different M are: N_2:He:Ar:SO_2=1.0:0.45:0.87:56.	SE	220-353	1.2(16)		1130	3	
78 TRO M=Ar. Derived by fitting a modified Arrhenius expression to the experimental data of 75 WES/DEH and 79 AST/GLA.	DE	250-2500	4.9(18)	-4	2646	3	

$O + SO_2 + M \rightarrow SO_3 + M$ -- Continued

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
79 AST/GLA M=Ar. Shock wave decomposition of SO_3. Monitored SO_2 formed by uv absorption. Calculated k for the reverse rn. ($O+SO_2+M \rightarrow SO_3+M$) using the equilibrium constant.	EX	1700-2500	1.06(13)		-7870	3	
80 BAU/COX *) M=Ar. Estimated error factor: 3 for 200-500K, 2 for 300K.	SE	200-2500	2.8(19)	-3.75	2650	3	*)
84 ATK/LLO M=N_2 and M=O_2	SE	298	4.9(14)			3	1.3
M=N_2 and M=O_2 The third body efficiencies of N_2 and O_2 are assumed equal.	SE	300-440	(1.5±0.4)(16)		1009	3	
84 BAU/COX M=N_2 and M=O_2	SE	298	5.1(14)			3	2
M=N_2 and M=O_2	SE	200-400	1.5(16)		1000	3	
Recommended value of k for M=Ar	RE	299	3.7(14)			3	1.3
Recommended values of Arrhenius A and B for M=Ar	RE	299-440	1.1(16)		1010±200	3	1.5
Recommended values of Arrhenius A and B for M=Ar	RE	1700-2500	1.06(13)		-7870	3	2
Recommended value of k for M=He	RE	298	3.5(14)			3	1.3
Recommended values of Arrhenius A and B for M=He	RE	248-415	4.0(16)		1400±200	3	1.5

Based recommendations on the data of 78 ATK/PIT, 75 WES/DEH2 and (for 1700-2500K) of 79 AST/GLA. Tentatively recommended relative third body efficiencies at 298K are $Ar:He:N_2:O_2:N_2O:SO_2$= 1.0:0.9:1.3:1.3:3:10, within about 30% and, for SO_2, up to a factor of 3.

Arrhenius plots for $O+SO_2+M \rightarrow$products are shown in Fig. 1 (1a for M=He and 1b for M=Ar (at 299-440K)).

References for reaction $O + SO_2 + M \rightarrow SO_3 + M$

58 KAU Kaufman, F., "The air afterglow and its use in the study of some reactions of atomic oxygen," Proc. Roy. Soc. A **247**, 123 (1958).

65 LEV/MER Levy, A., and Merryman, E. L., "The microstructure of hydrogen sulphide flames," Combustion and Flame **9**, 229 (1965).

65 WEB/WAL Webster, P., and Walsh, A.D., "The effect of sulfur dioxide on the second pressure limit of explosion of hydrogen-oxygen mixtures," Tenth Symposium (International) on Combustion, p. 463, The Combustion Institute (1965).

66 CAD/POW Cadle, R.D., and Powers, J.W., "Some aspects of atmospheric chemical reactions of atomic oxygen," Tellus **18**, 176 (1966)

66 HAL/THR Halstead, C.J. and Thrush, B.A., "The kinetics of elementary reactions involving the oxides of sulphur. II. Chemical reactions in the sulphur dioxide afterglow," Proc. Roy. Soc. A **295**, 363 (1966).

66 JAF/KLE Jaffe, S., and Klein, F.S., "Photolysis of NO_2 in presence of SO_2 at 3660A," Trans. Faraday Soc. **62**, 2150 (1966).

References for reaction $O + SO_2 + M \rightarrow SO_3 + M$ -- Continued

67 MUL/STE	Mulcahy, M.F.R., Steven, J.R., and Ward, J.C., "The kinetics of reaction between oxygen atoms and sulfur dioxide: an investigation by electron spin resonance spectrometry," J. Phys. Chem. 71, 2124 (1967).
69 MUL/STE	Mulcahy, M.F.R., Steven, J.R., Ward, J.C., and Williams, D.J., "Kinetics of interaction of oxygen atoms with sulfur oxides," Twelfth Symposium (International) on Combustion, p. 323, The Combustion Institute, 1969.
69 NET/STI	Nettleton, M.A., and Stirling, R., "Formation and decomposition of sulfur trioxide in flames and burned gases," Twelfth Symposium (International) on Combustion, p. 635, The Combustion Institute (1969).
71 HEI/WOO	Heicklen, J., Wood, W.P., Olszyna, K.J., and Cehelnik, E., "The reactions of unstable intermediates in the oxidation of CS_2," in 'Chemical Reactions in Urban Atmospheres' (C.S. Tuesday, editor), p. 191 (1971).
71 TIM/LEF	Timmons, R.B., LeFevre, H.F., and Hollinden, G.A., "Reactions of sulfur dioxide of possible atmospheric significance," in 'Chemical Reactions in Urban Atmospheres' (C.S. Tuesday, editor), p. 159 (1971).
73 SCH	Schofield, K., "Evaluated chemical kinetic rate constants for various gas phase reactions," J. Phys. Chem. Ref. Data 2, 25 (1973).
74 ATK/PIT	Atkinson, R., and Pitts, J.N., Jr., "Rate constants for the reaction of $O(^3P)$ atoms with SO_2 ($M=N_2O$) over the temperature range 299-392K," Chem. Phys. Lett. 29, 28 (1974).
74 DAV	Davis, D.D., "A kinetics review of atmospheric reactions involving HxOy compounds," Can. J. Chem. 52, 1405 (1974).
75 WES/DEH2	Westenberg, A.A., and deHaas, N., "Rate of the reaction $O + SO_2 + M \rightarrow SO_3 + M$," J. Chem. Phys. 63, 5411 (1975).
76 BAU/DRY	Baulch, D.L., Drysdale, D.D., Duxbury, J., and Grant, S.J., "Homogeneous gas phase reactions of the O_2-O_3 system, the CO-O_2-H_2 system, and of sulphur-containing species," in 'Evaluated Kinetic Data for High Temperature Reactions', Vol. 3, Butterworths, London (1976).
78 ATK/PIT	Atkinson, R., and Pitts, J.N., Jr., "Kinetics of the reaction $O(^3P) + SO_2 + M \rightarrow SO_3 + M$ over the temperature range of 299-440K," Int. J. Chem. Kinet. 10, 1081 (1978).
78 HAM/GAR	Hampson, R.F., Jr., and Garvin, D., editors, "Reaction rate and photochemical data for atmospheric chemistry - 1977," Nat. Bur. Stand. Spec. Publ. 513 (1978).
78 TRO	Troe, J., "Atom and radical recombination reactions," Ann. Rev. Phys. Chem. 29, 223 (1978).
79 AST/GLA	Astholz, D.C., Glanzer, K., and Troe, J., "The spin-forbidden dissociation-recombination reaction $SO_3 = SO_2 + O$," J. Chem. Phys. 70, 2409 (1979).
80 BAU/COX	Baulch, D.L., Cox, R.A., Hampson, R.F., Jr., Kerr, J.A., Troe, J., and Watson, R.T., "Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry," J. Phys. Chem. Ref. Data 9, 295 (1980).
84 ATK/LLO	Atkinson, R., and Lloyd, A.C., "Evaluation of kinetic and mechanistic data for modeling of photochemical smog," J. Phys. Chem. Ref. Data 13, 315 (1984).
84 BAU/COX	Baulch, D.L., Cox, R.A., Hampson, R.F., Jr., Kerr, J.A., Troe, J., and Watson, R.T., "Evaluated kinetic and photochemical data for atmospheric chemistry: supplement II," J. Phys. Chem. Ref. Data 13, 1259 (1984).

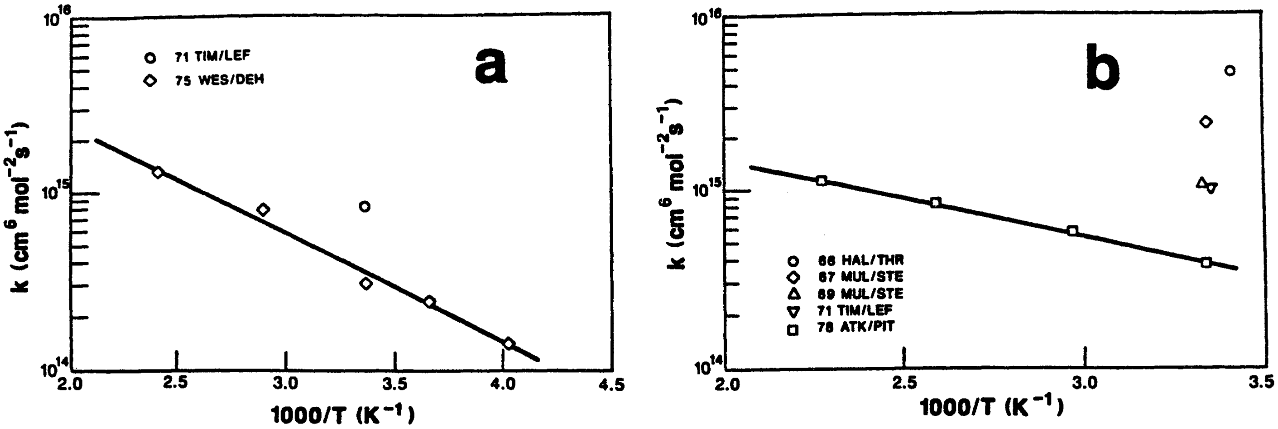

Fig. 1. Arrhenius plots for O+SO$_2$+M→products with M=He (1a) and M=Ar at 299-440K (1b). The lines are calculated using the recommended A and B values.

$O + SO_2 \rightarrow SO + O_2$

O + Sulfur dioxide

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
73 WAG Derived from the rate parameters (A=1.3(12), B=3986) for the reverse reaction and the equilibrium constant.	DE		5(12)		9813	2	
76 BAU/DRY Based on the recommended rate constant expression for the reverse reaction (76 BAU/DRY) and the equilibrium constant expression of 73 SCH.	SE	440-2100	6.80(12)	-0.511	9980	2	
78 HAM/GAR Accepted recommendation of 76 BAU/DRY.	SE	440-2100	7.3(12)	-0.5	9980	2	1.8

O + SO_2 → SO + O_2 -- Continued

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
80 SLA/GRI Reflected shock waves in mixture of $SO_2/N_2O/Ar$. P=2-5 atm. Monitored decay of SO_2 by IR emission at 7.347 microns. [O], used to calculate k values, computed from a model of 8 reactions.	EX	3320-3760	(3.8±0.5)(11)			2	
Recommended values of Arrhenius A and B Based on the indirectly derived parameters of 73 WAG and 76 BAU/DRY. Additional experimental work is needed.	RE	440-3000	5(12)		9800	2	3

References for reaction O + SO_2 → SO + O_2

73 WAG Wagner, H.Gg., "Elementary reactions in the combustion of small inorganic molecules," Fourteenth Symposium (International) on Combustion, p. 27, The Combustion Institute (1973).

76 BAU/DRY Baulch, D.L., Drysdale, D.D., Duxbury, J., and Grant, S.J., "Homogeneous gas phase reactions of the O_2-O_3 system, the CO-O_2-H_2 system, and of sulphur-containing species," in 'Evaluated Kinetic Data for High Temperature Reactions', Vol. 3, Butterworths, London (1976).

78 HAM/GAR Hampson, R.F., Jr., and Garvin, D., editors, "Reaction rate and photochemical data for atmospheric chemistry - 1977," Nat. Bur. Stand. Spec. Publ. 513 (1978).

80 SLA/GRI Slack, M., and Grillo, A., "Rate coefficient measurements for SO_2 + O = SO + O_2," J. Chem. Phys. **73**, 987 (1980).

O + SO_3 → products

O + Sulfur trioxide

The product is always assumed to be SO_2+O_2. (See 75 WES/DEH1 for suggestion that rn. is third order, i.e. $O+SO_3+M \rightarrow SO_2+O_2+M$).

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
58 KAU Discharge flow. O formed by microwave discharge in O_2 and monitored by O+NO chemiluminescence. No reaction was detectable between O and SO_3 in the gas phase, and the estimate of B is a lower limit. SO_3 was observed to change the rate of recombination of O on the reactor walls.	EX	300			≥3500		

$O + SO_3 \rightarrow$ products -- Continued

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
62 REU/LIN Reference rn. $O+SO_2 \rightarrow SO_3$ (assumed to be bimolecular). Thermal decomposition of N_2O mixed with SO_2 and either Ar, He, or CO_2. $[SO_2]$ determined by uv absorption. Monitored total pressure (up to about 500 Torr).	RL	961	0.16			2/2	
65 FEN/JON	RL	1600	5(-5)			2/2	
	RN	1600	1(12)			2	
Microprobe sampling of $H_2S/H_2/O_2$ flame. Mass spec. analyses. Reference rn. $O+SO_2+M \rightarrow SO_3+M$. k_{ref} taken as 3(16) $cm^6mol^{-2}s^{-1}$. The k values are undefined "averages" for $O+SO_3$ and $H+SO_3$ rns. P=60-200 Torr.							
71 MER/LEV Microprobe sampling of $COS/O_2/N_2$ flames. Monitored $[SO_3]$ by wet analyses; other stable species by mass spec. Reference rn. is $O+SO_2+M \rightarrow SO_3+M$ (A=2.4(17)$cm^6mole^{-2}s^{-1}$, B=1258 K).	RN	1480-1550	2.8(14)		6039	2	
71 MER/LEV Microprobe sampling of $H_2S/O_2/N_2$ flames, using the same procedure as in preceding data entry. Slightly larger k values are obtained than from the COS flame, possibly due to additional loss of SO_3 by reaction with H.	RN	1240-1340	6.5(14)		5435	2	
72 JAC/WIN Discharge flow. O formed by microwave discharge in N_2 followed by $N+NO \rightarrow O+N_2$. Reaction is "cold" quenched". k is based on SO_2 yield and measured [O] and $[SO_3]$. P=2 Torr. (A is recalculated).	EX	300-500	1.3(8)		500	2	
73 SCH Evaluation was based on only one set of data, 71 MER/LEV, which was considered questionable.	SE	1480-1550	2.8(14)		6039	2	

Recommendation is not warranted. Reaction order is not certain: 75 WES/DEH1 found more recently that reaction may be third order (see data sheet for rn. $O+SO_3+M$). Also, their second order k(298) at 2 Torr is several thousand times larger than that of 72 JAC/WIN. Furthermore, 75 WES/DEH1 find that B=-785, while 72 JAC/WIN find that B=500. 76 BAU/DRY found also that no recommendation was possible. Further study is needed.

References for reaction O + SO_3 → products

58 KAU Kaufman, F., "The air afterglow and its use in the study of some reactions of atomic oxygen," Proc. Roy. Soc. A 247, 123 (1958).

62 REU/LIN Reuben, B.G., Linnett, J.W., and Barber, M., "A new method of examining the reactions of oxygen atoms," Eighth Symposium (International) on Combustion, p. 97, The Combustion Institute (1962).

65 FEN/JON Fenimore, C.P., and Jones, G.W., "Sulfur in the burnt gas of hydrogen-oxygen flames," J. Phys. Chem. 69, 3593 (1965).

71 MER/LEV Merryman, E.L, and Levy, A., "Sulfur trioxide flame chemistry - H_2S and COS flames," Thirteenth Symposium (International) on Combustion, p. 427, The Combustion Institute (1971).

72 JAC/WIN Jacob, A., and Winkler, C.A., "Kinetics of the reactions of oxygen atoms and nitrogen atoms with sulphur trioxide," J. Chem. Soc. Faraday 1 68, 2077 (1972).

73 SCH Schofield, K., "Evaluated chemical kinetic rate constants for various gas phase reactions," J. Phys. Chem. Ref. Data 2, 25 (1973).

75 WES/DEH1 Westenberg, A.A., and deHaas, N., "Rate of the O + SO_3 reaction," J. Chem. Phys. 62, 725 (1975).

O + SO_3 + M → SO_2 + O_2 + M

O + Sulfur trioxide

Reference Code, Notes		Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
75 WES/DEH1	(M=He P=0.75-5.8 Torr)	EX	298-507	5.0(16)		-785	3	
	(M=N_2)	EX	298	1.0(18)			3	
	(M=SO_3 k_{rel}=k/k(M=He))	RL	298	<10			3/3	

Discharge flow reactor with ESR detection of O.

Recommendation: For reasons given for the previous rn. (O+SO_3→products) no recommendation is warranted. Additional experimental data are required.

Reference for reaction O + SO_3 + M → SO_2 + O_2 + M

75 WES/DEH1 Westenberg, A.A., and deHaas, N., "Rate of the O + SO_3 reaction," J. Chem. Phys. 62, 725 (1975).

$O + SH \rightarrow H + SO$

O + Mercapto

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
69 FAI/THR	RL	298	12			2/2	
	RN	298	1.8(14)			2	
Reference rn. $H + SH \rightarrow H_2 + S$. P = 0.9 Torr. Discharge flow. $H + H_2S$ rn. in presence of O_2. O formed by the secondary reaction $S+O_2 \rightarrow SO+O$. Rate constant is based on the [O] and [SO], determined from O+NO and O+SO chemiluminescences. To calculate RN used k_{ref}=1.5(13) (76 BAU/DRY).							
73 SCH	SE	295	1.2(14)			2	
Only one reported value (private communication, published subsequently in 75 CUP/GLA).							
75 CUP/GLA	RL	295	6.5±0.7			2/2	
	RN	295	(9.6±3)(13)			2	
Reference rn. $H + SH \rightarrow$ products. Discharge flow. ESR detection of H, O and OH. Based on an assumed rn. mechanism, the ratio [H]/[O] was identified with k(O+SH)/k(H+SH). In separate experiments found k_{ref}=(1.5±0.5)(13).							
85 DEM/MAR	SE	298	9.6(13)			2	5.0
Accepted RN (the Normalized k) of 75 CUP/GLA.							
Recommended value of k	RE	298	1.4(14)			2	3
Obtained as the average of the RN (the Normalized k) values of FAI/THR and 75 CUP/GLA.							

References for reaction $O + SH \rightarrow H + SO$

69 FAI/THR	Fair, R.W., and Thrush, B.A., "Reaction of hydrogen atoms with hydrogen sulphide in the presence of molecular oxygen," Trans. Faraday Soc. 65, 1557 (1969).
73 SCH	Schofield, K., "Evaluated chemical kinetic rate constants for various gas phase reactions," J. Phys. Chem. Ref. Data 2, 25 (1973).
75 CUP/GLA	Cupitt, L.T., and Glass, G.P., "Reactions of SH with atomic oxygen and hydrogen," Int. J. Chem. Kinet. Symp. 1, 39 (1975).
76 BAU/DRY	Baulch, D.L., Drysdale, D.D., Duxbury, J., and Grant, S.J., "Homogeneous gas phase reactions of the O_2-O_3 system, the CO-O_2-H_2 system, and of sulphur-containing species," in 'Evaluated Kinetic Data for High Temperature Reactions', Vol. 3, Butterworths, London (1976).
85 DEM/MAR	NASA Panel for Data Evaluation: DeMore, W.B., Margitan, J.J., Molina, M.J., Watson, R.T., Golden, D.M., Hampson, R.F., Kurylo, M.J., Howard, C.J., and Ravishankara, A.R., "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling. Evaluation number 7," J.P.L. Publ. 85-37 (1985).

O + SH → OH + S

O + Mercapto

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
68 MAY/SCH Used Bond Energy-Bond Order (BEBO) technique.	TH	298-2500	1.0(13)	0.67	956	2	
73 SCH Based on the theoretical estimate of Mayer and Schieler (see 68 MAY/SCH, the preceding entry).	SE	298-2500	1.0(13)	0.67	956	2	

Recommendation: No k values are recommended because the only available rate data have been obtained by a BEBO calculation. Until experimental values are obtained, the theoretical BEBO values of 68 MAY /SCH may be provisionally used, possibly with an uncertainty of an order of magnitude.

References for reaction O + SH → OH + S

68 MAY/SCH	Mayer, S.W., and Schieler, L., "Computed activation energies and rate constants for forward and reverse transfers of hydrogen atoms," J. Phys. Chem. 72, 236 (1968).
73 SCH	Schofield, K., "Evaluated chemical kinetic rate constants for various gas phase reactions," J. Phys. Chem. Ref. Data 2, 25 (1973).

O + H_2S → products

O + Hydrogen sulfide

The rn. product usually assumed is OH+SH. Two alternative products (SO+H_2 and HSO+H) are discussed further below (see the data sheets for rns. O+H_2S→SO+H_2 and O+H_2S→HSO+H).

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
65 LEV/MER	EX	1260	2.3(14)			2	
	EX	1350	1.3(15)			2	
Microprobe study of $H_2S/O_2/N_2$ or of $H_2S/O_2/Ar$ flames. Used mass spec. to analyze for O_2, H_2S, H_2O, H_2, and SO_2, and wet analysis for SO + SO_2 and SO_3. Rate constants calculated from rates of H_2S consumption.							
66 LIU/DON *) Room temperature. P=0.38-0.53 Torr. Discharge flow. Mass spec. detection of O, H_2S, and products. k calculated from the loss of H_2S and the chain length of 5±1.5 for loss of H_2S.	EX	*)	(2.4±1.2)(10)			2	

$O + H_2S \rightarrow$ products -- Continued

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
67 MER/LEV Microprobe sampling of $H_2S/O_2/N_2$ flames using mass spec. Rate constant calculated from rates of formation of H_2S, H_2O and H_2, and the calculated equilibrium O concentration. P=76 Torr.	EX	1055	2.8(13)			2	
70 CUP/GLA Discharge flow. ESR detection of O, SO, and H. Rate constant derived by adjusting it and three other k values to obtain the best fit of a 7 rn. mechanism to the experimental data. Revised k to 9.09(9) in 75 CUP/GLA.	DE	295	8.25(9)			2	
70 HOL/KUR Discharge flow. Monitored O atoms by ESR. Allowance was made for the assumed stoichiometry $d[O]/d[H_2S]=3.5\pm0.5$. P=1.38-2.25 Torr at 300 K.	EX	205-300	(1.74±0.40)(11)		755±50	2	
70 TAK Discharge flow. Monitored the afterglow of SO, SO_2, and O_2. Evaluated k from consumption of H_2S, correcting for stoichiometry ($d[O]/d[H_2S] = 1.2$) and the chain decomposition of H_2S.	EX	293	2.12(10)			2	
73 SCH	SE	200-350	3.8(11)		921±126	2	<2
75 CUP/GLA Revised k of 70 CUP/GLA.	DE	295	9.09(9)			2	
76 WHY/TIM Flash photolysis of $Ar/H_2S/O_2$ mixtures. O monitored by resonance fluorescence. P=10-400 Torr.	EX	263-495	(4.36±0.64)(12)		1661±50	2	
78 HAM/GAR	SE	263-495	4.36(12)		1660	2	1.25
78 SLA/BAI P=0.7-2.1 Torr at 496 K. Discharge flow. Photoionization mass spec. Decay of H_2S monitored in excess O atoms. A and B (not reported by the authors) were calculated (87 SIN/CVE) from the 19 k values listed in the supplementary material of 78 SLA/BAI.	EX	280-497	(1.96±0.20)(13)		2019±39	2	

$O + H_2S \rightarrow$ **products** -- Continued

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
79 SIN/IRW	EX	297-502	(1.56±0.83)(13)		2171±202	2	
Phase shift technique, with modulated [O] measured by O+NO chemiluminescence. O generated by Hg-photosensitized decomposition of N_2O.							
84 BAU/COX	SE	298	1.3(10)			2	2
	SE	290-500	8.4(12)		1920±750	2	
For discussion see 82 BAU/COX.							
85 DEM/MAR	SE	298	1.3(10)			2	1.7
	SE		6.0(12)		1810±550	2	
Selection based on 79 SIN/IRW and 76 WHY/TIM.							
Recommended value of k	RE	298	1.5(10)			2	1.3
Recommended values of Arrhenius A and B	RE	263-502	6.0(12)		1789±200	2	1.8

82 BAU/COX and 85 DEM/MAR reviews give the least squares fit of the preferred data of 76 WHY/TIM and 79 SIN/IRW, which give the same values within experimental error for 330<T<500K, but those of 79 SIN/IRW are lower at lower T. Higher T data (>1000K) of other workers, considered less reliable, are scattered and lie significantly above the fitted line. The present recommended values have been derived by fitting the Arrhenius equation to the data of 76 WHY/TIM and 79 SIN/IRW.

Arrhenius plots for the reaction $O+H_2S \rightarrow$products are shown in Fig. 2.

References for reaction $O + H_2S \rightarrow$ products

65 LEV/MER Levy, A., and Merryman, E. L., "The microstructure of hydrogen sulphide flames," Combustion and Flame 9, 229 (1965).

66 LIU/DON Liuti, G., Dondes, S., and Harteck, P., "The reaction of hydrogen sulfide and atomic oxygen," J. Am. Chem. Soc. 88, 3212 (1966).

67 MER/LEV Merryman, E.L., and Levy, A., "Kinetics of sulfur-oxide formation in flames: II. Low pressure H_2S flames," J. Air Pollution Control Association 17, 800 (1967).

70 CUP/GLA Cupitt, L.T., and Glass, G.P., "Reaction of atomic oxygen with hydrogen sulfide," Trans. Faraday Soc. 66, 3007 (1970).

70 HOL/KUR Hollinden, G.A., Kurylo, M.J., and Timmons, R.B., "Electron spin resonance study of the reaction of $O(^3P)$ atoms with H_2S," J. Phys. Chem. 74, 988 (1970).

70 TAK Takahashi, S., "The study of the reaction of hydrogen sulphide with atomic oxygen using emission spectrum," Mem. Nat. Def. Acad. Japan 10, 369 (1970).

73 SCH Schofield, K., "Evaluated chemical kinetic rate constants for various gas phase reactions," J. Phys. Chem. Ref. Data 2, 25 (1973).

75 CUP/GLA Cupitt, L.T., and Glass, G.P., "Reactions of SH with atomic oxygen and hydrogen," Int. J. Chem. Kinet. Symp. 1, 39 (1975).

76 WHY/TIM Whytock, D.A., Timmons, R.B., Lee, J.H., Michael, J.V., Payne, W.A., and Stief, L.J., "Absolute rate of the reaction of $O(^3P)$ with hydrogen sulfide over the temperature range 263 to 495K," J. Chem. Phys. 65, 2052 (1976).

References for reaction O + H_2S → products -- Continued

78 HAM/GAR Hampson, R.F., Jr., and Garvin, D., editors, "Reaction rate and photochemical data for atmospheric chemistry - 1977," Nat. Bur. Stand. Spec. Publ. 513 (1978).

78 SLA/BAI Slagle, I.R., Baiocchi, F., and Gutman, D., "Study of the reactions of oxygen atoms with hydrogen sulfide, methanethiol, ethanethiol, and methyl sulfide," J. Phys. Chem. 82, 1333 (1978).

79 SIN/IRW Singleton, D.L., Irwin, R.S., Nip, W.S., and Cvetanovic, R.J., "Kinetics and mechanism of the reaction of oxygen atoms with hydrogen sulfide," J. Phys. Chem. 83, 2195 (1979).

82 BAU/COX Baulch, D.L., Cox, R.A., Crutzen, P.J., Hampson, R.F., Jr., Kerr, J.A., Troe, J., and Watson, R.T., "Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement 1," J. Phys. Chem. Ref. Data 11, 327 (1982).

84 BAU/COX Baulch, D.L., Cox, R.A., Hampson, R.F., Jr., Kerr, J.A., Troe, J., and Watson, R.T., "Evaluated kinetic and photochemical data for atmospheric chemistry: supplement II," J. Phys. Chem. Ref. Data 13, 1259 (1984).

85 DEM/MAR NASA Panel for Data Evaluation: DeMore, W.B., Margitan, J.J., Molina, M.J., Watson, R.T., Golden, D.M., Hampson, R.F., Kurylo, M.J., Howard, C.J., and Ravishankara, A.R., "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling. Evaluation number 7," J.P.L. Publ. 85-37 (1985).

87 SIN/CVE Singleton, D.L., and Cvetanovic, R.J., The present evaluation.

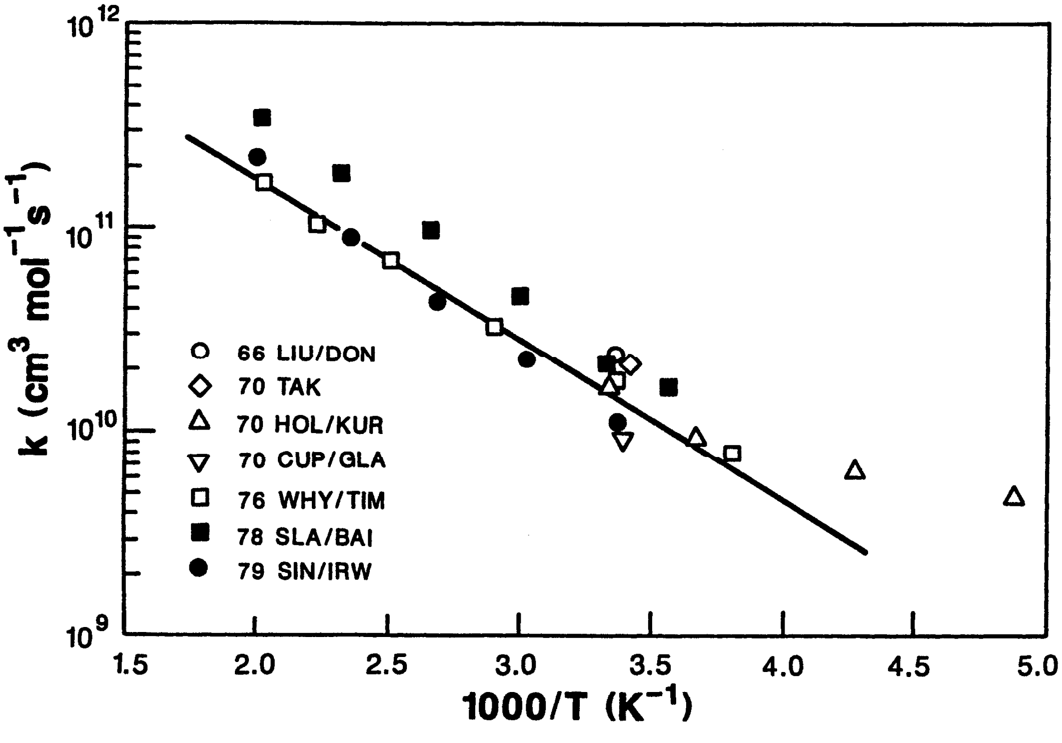

Fig. 2. Arrhenius plots for the reaction O+H_2S→products. The line is calculated using the recommended A and B values.

$O + D_2S \rightarrow OD + SD$

O + Deuterium sulfide

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
76 WHY/TIM Flash photolysis of Ar, D_2S, O_2 mixtures with time-resolved resonance fluorescence detection of O atoms. P=10-200 Torr.	EX	298-450	(6.32±3.4)(12)		2144±156	2	
Recommended value of k	RE	298	4.7(9)			2	1.4
Recommended values of Arrhenius A and B	RE	298-450	6.3(12)		2144±200	2	2
Based on the only data available (76 WHY/TIM). Additional determinations would be useful.							

Reference for reaction $O + D_2S \rightarrow OD + SD$

76 WHY/TIM Whytock, D.A., Timmons, R.B., Lee, J.H., Michael, J.V., Payne, W.A., and Stief, L.J., "Absolute rate of the reaction of $O(^3P)$ with hydrogen sulfide over the temperature range 263 to 495K," J. Chem. Phys. 65, 2052 (1976).

$O + H_2S \rightarrow SO + H_2$

O + Hydrogen sulfide

A higher temperature channel in the rn. $O+H_2S \rightarrow$products. See also the rn. $O+H_2S \rightarrow HSO+H$.

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
67 BRA/DOB *) Reference rn. $O+H_2S \rightarrow$ products. Arrh. A not given. Shock tube-Absorption spec. $H_2S/O_2/Ar$ mixtures. This channel is proposed to account for increased SO_2 at high T. Based on the difference in the induction times of OH and SO_2 at low and high T, a value of $E-E_{ref}$ = 8 kcal/mole (B=4026 K) is proposed.	RL	1350-2450	*)		4026	2/2	
81 FRE/LEE Reflected shock waves, measurement of induction time modeling of 57 reactions. Identical k values are derived for another rn. channel (see 81 FRE/LEE in the following rn.).	DE	1050-2000	1.0(13)		5032	2	

Recommendation: This is evidently an insignificant pathway at room temp. There are no direct determinations on which to base a recommended value. The two reported values are indirectly derived in studies of complex systems at high temperatures (1050-2450K). More data are needed.

References for reaction $O + H_2S \rightarrow SO + H_2$

67 BRA/DOB Bradley, J.N., and Dobson, D.C., "Oxidation of hydrogen sulfide in shock waves. I. Absorption studies of OH and SO_2 in H_2S-O_2-Ar mixtures," J. Chem. Phys. 46, 2865 (1967).

81 FRE/LEE Frenklach, M., Lee, J.H., White, J.N., and Gardiner, W.C., Jr., "Oxidation of hydrogen sulfide," Combustion and Flame 41, 1 (1981).

$O + H_2S \rightarrow HSO + H$

O + Hydrogen sulfide

A potental minor channel in the rn. $O+H_2S \rightarrow$products. See also the rn. $O+H_2S \rightarrow SO+H_2$.

A channel in the rn. $O+H_2S \rightarrow$products due to attack on S rather than on H. Quantitative determination of the "branching ratio" for O addition to S as opposed to H abstraction is difficult (79 SIN/IRW; 82 SIN/PAR) because rates of some potentially involved elementary reactions are not known.

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
79 SIN/IRW *) Room temperature. O generated by Hg-photosensitized decomposition of N_2O. Reference rn. $O+H_2S \rightarrow$products. Relative k based on collection of noncondensable gases formed (H_2 and N_2) and their GC analysis. The upper limit may be as high as 0.2 (82 SIN/PAR).	RL	*)	<0.11			2/2	
81 FRE/LEE Reflected shock waves, measurement of induction time modeling of 57 reactions. Identical k values are derived for another rn. channel (see 81 FRE/LEE in the preceding rn.).	DE	1050-2000	1.0(13)		5032	2	
81 CLE/DAV Crossed molecular beam method, with angular resolved mass spec. Reaction cross section for HSO formation as function of translational energy of the reactants. Value given for B is the threshold translational energy, not the Arrhenius activation energy. (See 82 DAV/CLE).	EX				1683±240	2	
82 DAV/CLE Crossed molecular beam method, with angular resolved mass spec. Reaction cross section for HSO formation as function of translational energy of the reactants. Value given for B is the threshold translational energy, not the Arrhenius activation energy. (See 81 CLE/DAV).	EX				1683±240	2	

+ $H_2S \rightarrow HSO + H$ -- Continued

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
82 SIN/PAR An upper-limit value for the branching ratio k/k($O+H_2S \rightarrow$products).	RL	298	<0.2			2/2	1.1
Recommended branching ratio k/k($O+H_2S \rightarrow$products) Based on the upper-limit value of 82 SIN/PAR.	RE	298	<0.2			2/2	1.1

References for reaction $O + H_2S \rightarrow HSO + H$

79 SIN/IRW	Singleton, D.L., Irwin, R.S., Nip, W.S., and Cvetanovic, R.J., "Kinetics and mechanism of the reaction of oxygen atoms with hydrogen sulfide," J. Phys. Chem. 83, 2195 (1979).
81 CLE/DAV	Clemo, A.R., Davidson, F.E., Duncan, G.L., and Grice, R., "Translational energy threshold functions for oxygen atom reactions," Chem. Phys. Lett. 84, 509 (1981).
81 FRE/LEE	Frenklach, M., Lee, J.H., White, J.N., and Gardiner, W.C., Jr., "Oxidation of hydrogen sulfide," Combustion and Flame 41, 1 (1981).
82 DAV/CLE	Davidson, F.E., Clemo, A.R., Duncan, G.L., Browett, R.J., Hobson, J.H., and Grice, R., "Reactive scattering of a supersonic oxygen atom beam: O + H_2S," Molec. Phys. 46, 33 (1982).
82 SIN/PAR	Singleton, D.L., Paraskevopoulos, G., and Irwin, R.S., "Mechanism of the $O(^3P)$ + H_2S Reaction. Abstraction or Addition?," J. Phys. Chem. 86, 2605 (1986).

+ $H_2SO_4 \rightarrow$ products

+ Sulfuric acid

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
80 BAL/GOL *) Room temperature; H_2SO_4 liquid. #) Reaction probability per collison < 1.0(-6). Discharge flow with Knudsen cell reactor. Mass spec. detection of O. No measureable reaction, no detectable products.	EX	*)	#)			2/2	
Recommended value of k #) Reaction probability per collison < 1.0(-6). Based on the only data available (80 BAL/GOL). Additional experimental work is desirable.	RE	298	#)			2/2	

Reference for reaction $O + H_2SO_4 \rightarrow$ products

80 BAL/GOL Baldwin, A.C., and Golden, D.M., "Heterogeneous atmospheric reactions. 2. Atom and radical reactions with sulfuric acid," J. Geophys. Res. 85, 2888 (1980).

$O + CS \rightarrow$ products

O + Carbon monosulfide

The main and probably exclusive rn. channel is $O + CS \rightarrow CO + S$.

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
68 HOM/KRO An order of magnitude estimate of k quoted in the Abstract of the paper.	ES	1100	~1(14)			2	
71 HAN/SMI	RL	298	2.3			2/2	
Reference rn. $O+NO_2 \rightarrow NO+O_2$. Measured the effect of NO_2 on the vibrational emission intensities of CO. [RN value has been updated using k_{ref}= 5.6(12) (85 DEM/MAR)].	RN	298	1.3(13)			2	
73 SCH Based on the data (without a recommendation) of 71 HAN/SMI.	SE	298	8.4(12)			2	
75 SLA/GRA Discharge flow. CS formed by a dc discharge in CS_2, and O by microwave discharge in O_2 (or in N_2 followed by N+NO rn.). Decay of CS in excess O followed by photoionization mass spec.	EX	305	(1.24±0.08)(13)			2	
76 BAU/DRY *) No new recommedation. Suggest using Hancock and Smith's data (see 71 HAN/SMI).	SE		*)			2	
76 BID/BRE Flow tube technique. CS, produced by microwave discharge in a dilute CS_2/Ar stream, monitored by multipath uv absorption. Small [O] (<< [CS]) is maintained by rapid regeneration in the rn. $S + O_2 \rightarrow O + SO$. (See also 78 KOL).	EX	300	(1.35±0.22)(13)			2	

O + CS → products -- Continued

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
77 LIL/RIC	EX	150-300	(1.6±0.2)(14)		758±144	2	
	EX	298	1.26(13)			2	
Discharge flow. Mass spec. measurement of CO formation in excess CS and of CS disappearance in excess O. Also monitored S and O by ESR. CS made by a dc discharge (CS$_2$), and O by a microwave discharge (NO or O$_2$). [k(298K) calculated from the Arrhenius eqn.].							
78 HAM/GAR Accepted recommendation of 76 BAU/DRY.	SE	300	1.3(13)			2	1.6
78 KOL Flow tube technique. CS, produced by microwave discharge in a dilute CS$_2$/Ar stream, monitored by multipath uv absorption. Small [O] (<< [CS]) is maintained by rapid regeneration in the rn. S + O$_2$ → O + SO. (See also 76 BID/BRE).	EX	300	(1.35±0.22)(13)			2	
78 TAL/BUT Diffusion cloud ("diffusion flame") technique. O atoms formed by N+NO rn. CS consumption monitored by mass spec. P(He)=20 Torr.	EX	298	(1.3±0.13)(13)			2	
84 BAU/COX	SE	298	1.3(13)			2	1.25
	SE	150-300	1.6(14)		760±250	2	
For discussion see 80 BAU/COX.							
Recommended value of k	RE	298	1.2(13)			2	1.2
Recommended values of Arrhenius A and B	RE	156-305	1.5(14)		751±100	2	1.5

Based on the least squares fit of all the data in 156-305K range assuming linear Arrhenius plot.

Arrhenius plot for O+CS→products is shown in Fig. 3.

References for reaction O + CS → products

68 HOM/KRO Homann, K.H., Krome, G., and Wagner, H.Gg., "Schwefelkohlenstoff-oxydation, geschwindigkeit von elementarreaktionen. Teil 1," Ber. Bunsenges. Phys. Chem. 72, 998 (1968).

71 HAN/SMI Hancock, G., and Smith, I.W.M., "Infra-red chemiluminescence from vibrationally excited CO. Part 1. The reaction of atomic oxygen with carbon disulphide," Trans. Faraday Soc. 67, 2586 (1971).

73 SCH Schofield, K., "Evaluated chemical kinetic rate constants for various gas phase reactions," J. Phys. Chem. Ref. Data 2, 25 (1973).

75 SLA/GRA Slagle, I.R., Graham, R.E., Gilbert, J.R., and Gutman, D., "Direct determination of the rate constant for the reaction of oxygen atoms with carbon monosulphide," Chem. Phys. Lett. 32, 184 (1975).

References for reaction $O + CS \rightarrow$ products -- Continued

76 BAU/DRY Baulch, D.L., Drysdale, D.D., Duxbury, J., and Grant, S.J., "Homogeneous gas phase reactions of the O_2-O_3 system, the CO-O_2-H_2 system, and of sulphur-containing species," in 'Evaluated Kinetic Data for High Temperature Reactions', Vol. 3, Butterworths, London (1976).

76 BID/BRE Bida, G.T., Breckenridge, W.H., and Kolln, W.S., "A kinetic study of the very fast reaction: $O(^3P)+CS \rightarrow CO^*+S(^3P)$," J. Chem. Phys. 64, 3296 (1976).

77 LIL/RIC Lilenfeld, H.V., and Richardson, R.J., "Temperature dependence of the rate constant for the reaction between carbon monosulfide and atomic oxygen," J. Chem. Phys. 67, 3991 (1977).

78 HAM/GAR Hampson, R.F., Jr., and Garvin, D., editors, "Reaction rate and photochemical data for atmospheric chemistry - 1977," Nat. Bur. Stand. Spec. Publ. 513 (1978).

78 KOL Kolln, W.S., "Gas Phase Reactions of Carbon Monosulfide Studied by the Fast Flow Technique," Diss. Abst. Int. B 39, 771 (1978).

78 TAL/BUT V.L. Tal'roze, Butkovskaya, N.I., Larichev, M.N., Leipunskii, I.O., Morozov, I.I., Dodonov, A.F., Kudrov, B.V., Zelenov, V.V., and Raznikov, V.V., (Daly, N.R., editor) "Advances in the mass spectrometry of free radicals," Advances in Mass Spectrometry 7A, 693 (1978).

80 BAU/COX Baulch, D.L., Cox, R.A., Hampson, R.F., Jr., Kerr, J.A., Troe, J., and Watson, R.T., "Evaluated kinetic and Photochemical Data for Atmospheric Chemistry," J. Phys. Chem. Ref. Data 9, 295 (1980).

84 BAU/COX Baulch, D.L., Cox, R.A., Hampson, R.F., Jr., Kerr, J.A., Troe, J., and Watson, R.T., "Evaluated kinetic and photochemical data for atmospheric chemistry: supplement II," J. Phys. Chem. Ref. Data 13, 1259 (1984).

85 DEM/MAR NASA Panel for Data Evaluation: DeMore, W.B., Margitan, J.J., Molina, M.J., Watson, R.T., Golden, D.M., Hampson, R.F., Kurylo, M.J., Howard, C.J., and Ravishankara, A.R., "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling. Evaluation number 7," J.P.L. Publ. 85-37 (1985).

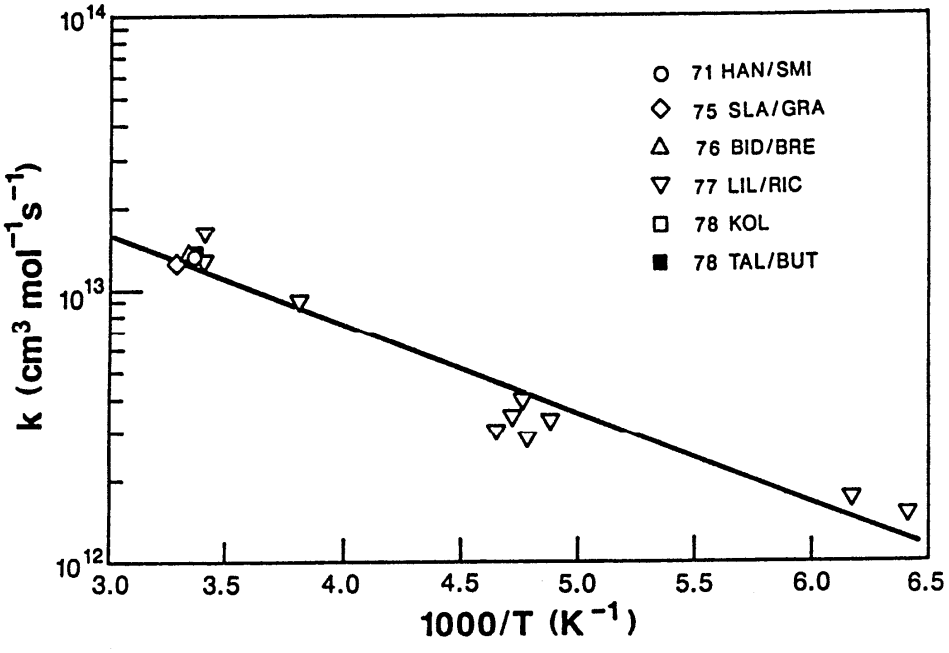

Fig. 3. Arrhenius plots for the reaction $O+CS \rightarrow$ products.
The line is calculated using the recommended A and B values.

O + CS_2 → products

O + Carbon disulfide

The main rn. product is CS+SO. For minor channels see rns. O+CS_2→COS+S and O+CS_2→CO+S_2.

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
67 CAL/SMI	EX	305-410	(6.3±1.3)(12)		302±151	2	
Flash photolysis-kinetic spectroscopy. O formed by photolysis of NO_2. The product CS monitored by uv spec. [The same values and some relative determinations reported also in 68 SMI].							
67 SMI	EX	305-410	(6.3±1.3)(12)		302±151	2	
Flash photolysis-kinetic spectroscopy. O formed by photolysis of NO_2. The reaction product CS monitored and SO detected by uv spec. 8% and 18% of rn. exothermicity goes into vibrational excitation of CS and SO, respectively. [See also 67 CAL/SMI and 68 SMI].							
68 HOM/KRO	EX	300-920	5(13)		956	2	
Discharge flow. Excess O formed by a microwave discharge in O_2 or in N_2 (followed by N+NO rn.). Decay of CS_2 and formation of SO followed by mass spec. P=3-6 Torr.							
68 SMI	EX	305-410	(6.3±1.3)(12)		302±151	2	
(Ref. rn. O + isobutene)	RL	298	0.32±0.03			2/2	
(Ref. rn. O + isobutene)	RL	410	0.40±0.05			2/2	
(Ref. rn. O + 1-butene)	RL	298	1.3±0.1			2/2	
(Ref. rn. O + 1-butene)	RL	410	1.2±0.1			2/2	
(Ref. rn. O + NO_2)	RL	298	0.71±0.2			2/2	
(Ref. rn. O + NO_2)	RL	410	0.65±0.2			2/2	
(Ref. rn. O + isobutene)	RN	298	3.26(12)			2	
(Ref. rn. O + 1-butene)	RN	298	3.25(12)			2	
(Ref. rn. O + NO_2)	RN	298	4.0(12)			2	
Flash photolysis-kinetic spectroscopy. O formed by photolysis of NO_2. The product CS monitored by uv spec. [See also 67 SMI and 67 CAL/SMI]. [The normalized (RN) values have been calculated (87 SIN/CVE) using the following k_{ref} values at 298 K: isobutene 1.02(13) (87 CVE), 1-butene 2.50(12) (87 CVE), NO_2 5.6(12) (85 DEM/MAR)].							

$O + CS_2 \rightarrow$ **products** -- Continued

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
69 WES/DEH Discharge flow. O formed by microwave discharge in O_2 or in N_2 (followed by N+NO rn.). Decay of O followed by ESR. Results were divided by a stoichiometric factor of 2. The reported A and B values were calculated by including the results of 68 SMI. P=1.93-2.10 Torr at 297 K. SO detected as a product by ESR.	EX	227-538	(1.2±0.2)(13)		528±50	2	
70 CAL/HED Flash Hg-photosensitized decomposition of N_2O in the presence of CS_2 to form O. Time dependence of CS determined by uv absorption. P=678 Torr.	EX	298	(2.2±0.2)(12)			2	
73 SCH Suggested error limits of ± 20% for 200-1000K.	SE	200-1000	1.2(13)		518±40	2	
74 SLA/GIL Discharge flow. O formed by microwave discharge in O_2 or in N_2 followed by N+NO rn. Decay of CS_2 in the presence of excess O followed by photoionization mass spec. P=1.4 Torr.	EX	302	(2.4±0.2)(12)			2	
75 WEI/TIM Discharge flow. O formed by microwave discharge of O_2 or of N_2 (followed by N+NO rn.). Decay of O in excess CS_2 followed by ESR. Results divided by the stoichiometric factor of 2.	EX	218-293	(1.66±0.23)(13)		644±35	2	
76 BAU/DRY Estimated uncertainty is 30% below 350 K, increasing to 100% at 1000 K.	SE	200-1000	2.2(13)		700	2	
77 GRA/GUT Discharge flow. O formed by microwave discharge in N_2 followed by N+NO rn. The decay of CS_2 in excess O followed by photoionization mass spec. The authors suggest that their data do not follow Arhhenius behavior. The values of A and B given above were calculated (87 SIN/CVE) assuming linear Arrhenius plots.	EX	249-500	(2.23±0.33)(13)		659±48	2	
78 HAM/GAR *) Accepted recommendation of 76 BAU/DRY. Suggested error factor of 1.4 for T<360K.	SE	200-1000	2.2(13)		700	2	*)

$O + CS_2 \rightarrow$ **products** -- Continued

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
78 TAL/BUT	EX	298	(1.4±0.14)(12)			2	
Diffusion cloud ("diffusion flame") technique. O atoms formed by N+NO rn. CS_2 consumption monitored by mass spec. P(He)=20 Torr.							
84 BAU/COX	SE	298	2.2(12)			2	1.6
	SE	200-500	1.9(13)		650±100	2	
Accepted the NASA evaluation (83 DEM/MOL). For $k(O+CS_2 \rightarrow SO+CS)/k(O+CS_2 \rightarrow products)$, i.e. for branching ratio, recommend a value ≥0.90.							
85 DEM/MAR	SE	298	2.2(12)			2	1.2
	SE		1.9(13)		650±150	2	
Averaged the room temp. data of 75 WEI/TIM, 69 WES/DEH, 74 SLA/GIL, 67 CAL/SMI, 70 CAL/HED, 68 HOM/KRO, and 77 GRA/GUT; averaged the B values of 75 WEI/TIM and 77 GRA/GUT; set the error in B to encompass the value of B of 69 WES/DEH.							
Recommended value of k	RE	298	2.3(12)			2	1.2
Recommended values of Arrhenius A and B	RE	218-920	3.55(13)		821±100	2	1.5

Based on the least squares fit of all data in the data sheet assuming linear Arrhenius plot.

Arrhenius plot for $O+CS_2 \rightarrow$products is shown in Fig. 4.

References for reaction $O + CS_2 \rightarrow$ products

67 CAL/SMI Callear, A.B., and Smith, I.W.M., "Measurement of the rate parameters for reaction of $O(2^3P)$ with carbon disulphide and olefines, by flash spectroscopy," Nature **213**, 382 (1967).

67 SMI Smith, I.W.M., "Experimental and computer studies of the kinetics and distribution of vibrational energy in both products of the reaction: $O(^3P) + CS_2 \rightarrow SO + CS$," Disc. Faraday Soc. **44**, 194 (1967).

68 HOM/KRO Homann, K.H., Krome, G., and Wagner, H.Gg., "Schwefelkohlenstoff-oxydation, geschwindigkeit von elementarreaktionen. Teil 1," Ber. Bunsenges. Phys. Chem. **72**, 998 (1968).

68 SMI Smith, I.W.M., "Rate parameters for reactions of $O(2^3P)$ with CS_2, NO_2, and olefins," Trans. Faraday Soc. **64**, 378 (1968).

69 WES/DEH Westenberg, A.A., and deHaas, N., "Atom-molecule kinetics using ESR detection. V. Results for O + OCS, $O + CS_2$, $O + NO_2$, and $H + C_2H_4$," J. Chem. Phys. **50**, 707 (1969).

70 CAL/HED Callear, A.B., and Hedges, R.E.M., "Flash spectroscopy with mercury resonance radiation. Part 1. An experimental method with microwave-pulse excitation," Trans. Faraday Soc. **66**, 605 (1970).

73 SCH Schofield, K., "Evaluated chemical kinetic rate constants for various gas phase reactions," J. Phys. Chem. Ref. Data **2**, 25 (1973).

References for reaction O + CS_2 → products -- Continued

74 SLA/GIL Slagle, I.R., Gilbert, J.R., and Gutman, D., "Kinetics of the reaction between oxygen atoms and carbon disulfide," J. Chem. Phys. 61, 704 (1974).

75 WEI/TIM Wei, C.-N., and Timmons, R.B., "ESR study of the kinetics of the reactions of $O(^3P)$ atoms with CS_2 and OCS," J. Chem. Phys. 62, 3240 (1975).

76 BAU/DRY Baulch, D.L., Drysdale, D.D., Duxbury, J., and Grant, S.J., "Homogeneous gas phase reactions of the O_2-O_3 system, the CO-O_2-H_2 system, and of sulphur-containing species," in 'Evaluated Kinetic Data for High Temperature Reactions', Vol. 3, Butterworths, London (1976).

77 GRA/GUT Graham, R.E., and Gutman, D., "Temperature dependence of rate constants and branching ratios for the reaction of oxygen atoms with carbon disulfide," J. Phys. Chem. 81, 207 (1977).

78 HAM/GAR Hampson, R.F., Jr., and Garvin, D., editors, "Reaction rate and photochemical data for atmospheric chemistry - 1977," Nat. Bur. Stand. Spec. Publ. 513 (1978).

78 TAL/BUT V.L. Tal'roze, Butkovskaya, N.I., Larichev, M.N., Leipunskii, I.O., Morozov, I.I., Dodonov, A.F., Kudrov, B.V., Zelenov, V.V., and Raznikov, V.V., (Daly, N.R., editor) "Advances in the mass spectrometry of free radicals," Advances in Mass Spectrometry 7A, 693 (1978).

84 BAU/COX Baulch, D.L., Cox, R.A., Hampson, R.F., Jr., Kerr, J.A., Troe, J., and Watson, R.T., "Evaluated kinetic and photochemical data for atmospheric chemistry: supplement II," J. Phys. Chem. Ref. Data 13, 1259 (1984).

85 DEM/MAR NASA Panel for Data Evaluation: DeMore, W.B., Margitan, J.J., Molina, M.J., Watson, R.T., Golden, D.M., Hampson, R.F., Kurylo, M.J., Howard, C.J., and Ravishankara, A.R., "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling. Evaluation number 7," J.P.L. Publ. 85-37 (1985).

87 CVE Cvetanovic, R.J., "Evaluated Chemical Kinetic Data for the Reactions of Atomic Oxygen $O(^3P)$ with Unsaturated Hydrocarbons," J. Phys. Chem. Ref. Data 16, 261 (1987).

87 SIN/CVE Singleton, D.L., and Cvetanovic, R.J., The present evaluation.

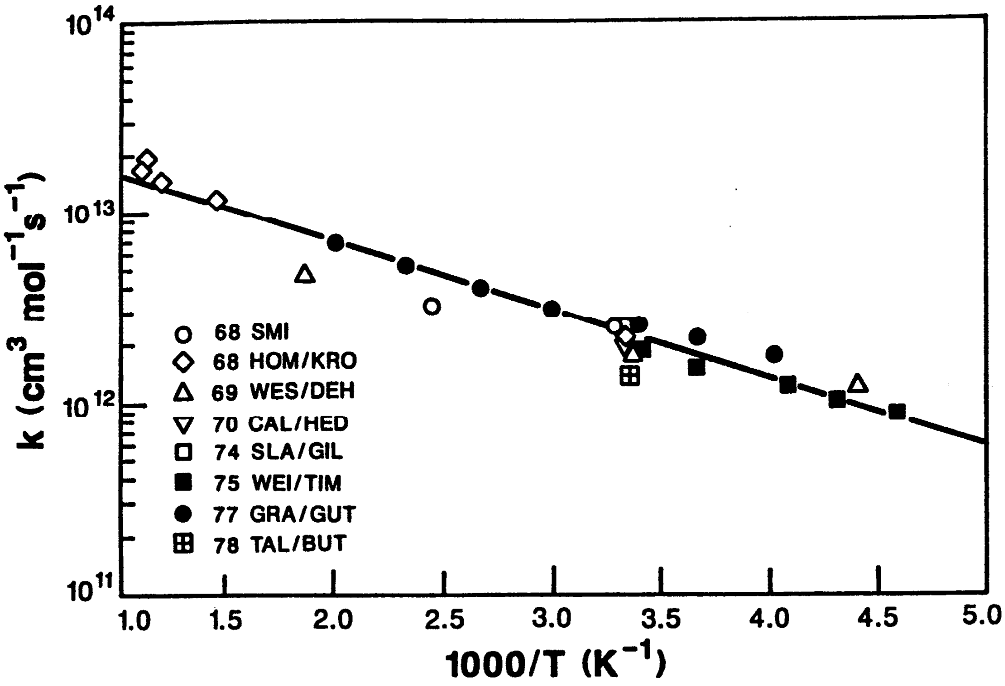

Fig. 4. Arrhenius plot for the reaction O+CS_2→products.
The line is calculated using the recommended A and B values.

$O + CS_2 \rightarrow COS + S$

O + Carbon disulfide

A channel in the rn. $O + CS_2 \rightarrow$ products.

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
68 HOM/KRO Discharge flow. Excess O formed by a microwave discharge in O_2 or in N_2 (followed by N+NO rn.). k value, based on rate of formation of COS, is approximate. The authors suggest that the branching ratio of the channel giving COS is 0.05 at 1100 K. P=3-6 Torr.	EX	1100	1(12)			2	
73 SCH Only one reported value (68 HOM/KRO). An estimated value at 298 K is given as 2.4(10).	SE	1100	1(12)			2	
74 SLA/GIL Discharge flow. O formed by microwave discharge in N_2 followed by N+NO rn. Decay of CS_2 and formation of COS followed by photoionization mass spec. P=1.4 Torr.	RL	302	0.093±0.008			2/2	
76 BAU/DRY The selected k value is based on the branching ratio reported by 74 SLA/GIL and the selected overall k value by 76 BAU/DRY.	SE	302	(2.2±1.1)(11)			2	
77 GRA/GUT *) k/k(overall) = (0.098±0.004) - (0.081±0.007). Discharge flow. O formed by microwave discharge in N_2 followed by N+NO rn. Decay of CS_2 and formation of COS followed by photoionization mass spec.	RL	249-500	*)			2/2	
Recommended value of k	RE	298	2.1(11)			2	1.3
Recommended values of Arrhenius A and B	RE	249-500	2.2(12)		701±100	2	2

Based on the data of 77 GRA/GUT for the branching ratio and the recommended Arrhenius parameters for the overall reaction of 87 SIN/CVE.

References for reaction $O + CS_2 \rightarrow COS + S$

68 HOM/KRO Homann, K.H., Krome, G., and Wagner, H.Gg., "Schwefelkohlenstoff-oxydation, geschwindigkeit von elementarreaktionen. Teil 1," Ber. Bunsenges. Phys. Chem. **72**, 998 (1968).

73 SCH Schofield, K., "Evaluated chemical kinetic rate constants for various gas phase reactions," J. Phys. Chem. Ref. Data 2, 25 (1973).

References for reaction $O + CS_2 \rightarrow COS + S$ -- Continued

74 SLA/GIL Slagle, I.R., Gilbert, J.R., and Gutman, D., "Kinetics of the reaction between oxygen atoms and carbon disulfide," J. Chem. Phys. 61, 704 (1974).

76 BAU/DRY Baulch, D.L., Drysdale, D.D., Duxbury, J., and Grant, S.J., "Homogeneous gas phase reactions of the O_2-O_3 system, the CO-O_2-H_2 system, and of sulphur-containing species," in 'Evaluated Kinetic Data for High Temperature Reactions', Vol. 3, Butterworths, London (1976).

77 GRA/GUT Graham, R.E., and Gutman, D., "Temperature dependence of rate constants and branching ratios for the reaction of oxygen atoms with carbon disulfide," J. Phys. Chem. 81, 207 (1977).

$O + CS_2 \rightarrow CO + S_2$

<u>O + Carbon disulfide</u>

A minor channel in the rn. $O+CS_2 \rightarrow$products.

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
79 HSU/SHA	RL	298	0.014±0.002			2/2	
	RN	298	(3.51±0.45)(10)			2	
Flash photolysis-CO laser absorption technique. The listed RL k is the branching ratio for the channel $O+CS_2 \rightarrow CO+S_2$. The normalized (RN) k is based on the ratio of 0.373 measured for the CO formed in the $O+CS_2$ and $O+C_2H_2$ rns. The RN value was obtained using $k(O+C_2H_2 \rightarrow CO+CH_2)$=9.4(10) (73 HER/HUI) and the branching ratio (the RL value) and $k(O+CS_2 \rightarrow$products)=2.53(12) (77 GRA/GUT).							
Recommended branching ratio $k/k(O+CS_2 \rightarrow$products)	RE	298	1.4(-2)			2/2	1.2
Recommended value of k	RE	298	3.5(10)			2	1.3
Based on the only data available (79 HSU/SHA). Additional determinations would be useful.							

References for reaction $O + CS_2 \rightarrow CO + S_2$

73 HER/HUI Herron, J.T., and Huie, R.E., "Rate Constants for the Reactions of Atomic Oxygen $O(^3P)$ with Organic Compounds in the Gas Phase," J. Phys. Chem. Ref. Data 2, 467 (1973).

77 GRA/GUT Graham, R.E., and Gutman, D., "Temperature dependence of rate constants and branching ratios for the reaction of oxygen atoms with carbon disulfide," J. Phys. Chem. 81, 207 (1977).

79 HSU/SHA Hsu, D.S.Y., Shaub, W.M., Burks, T.L, and Lin, M.C., "Dynamics of reactions of $O(^3P)$ atoms with CS, CS_2, and OCS," Chem. Phys. 44, 143 (1979).

O + COS → products

O + Carbon oxide sulfide

At lower T the only observed product is SO+CO. See rn. O+COS→CO_2+S for a higher T rn. channel.

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
65 ROL/REE O produced by discharge in O_2. Measured O+SO chemiluminescence. k is approximate, with no details given. No CO_2 observed by mass spec. A reference is made to the channel forming CO_2 and S, as being less than 0.001 of the channel forming CO and SO.	EX	298	6(9)			2	
65 SUL/WAR T not specified: presumably room temperature. Discharge flow. O formed by microwave discharge of O_2. Consumption of COS determined by mass spec. Consumption of O matched the formation of CO. P=0.3-1.3 Torr.	EX	*)	(5.5±0.8)(9)			2	
67 HOY/WAG Discharge flow. O formed by microwave discharge of N_2 (followed by the N+NO rn.). With excess COS, rate of decay of O measured by ESR and of formation of SO by molecular beam mass spec. Products CO, SO_2, S_2O, and S were detected by mass spec. P=0.5-5 Torr.	EX	290-465	1.2(14)		2919±50	2	
68 HOM/KRO Discharge flow. O formed by microwave discharge of O_2 or N_2 (followed by N+NO rn.). Decay of COS and formation of SO followed by molecular beam mass spec. in excess O. Measurements at 880-1150 K were combined with the earlier data (67 HOY/WAG) to obtain the listed Arrhenius parameters. Small amounts of CO_2, but not of SO_2, were observed as products.	EX	300-1150	6.5(13)		2768	2	
69 WES/DEH Discharge flow. O formed by microwave discharge of O_2 in He or Ar, or of N_2 (followed by N+NO rn.) and detected by ESR in excess COS. P=0.7-2.34 Torr at 297 K. SO detected as product; its yield, obtained using an adjusted value for final [SO], equalled consumption of O at 297 K. CO (but not CO_2) was detected as a product by by mass spectrometry.	EX	273-808	(1.9±0.7)(13)		2280±126	2	

O + COS → products -- Continued

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
71 KRE/SIM Ref. rn. O + 2-trifluoromethylpropene (TMP). O formed by Hg-photosensitized decomposition of N_2O. Monitored CO yield as a function of the ratio of TMP to COS. The normalized (RN) values were obtained using A_{ref}=9.09(12), B_{ref}=1117. P(N_2O)=490-657 Torr at 298 K.	RN	298-523	9.76(12)		2264	2	
72 BRE/MIL Discharge flow. O formed by microwave discharge of O_2 in He and monitored in excess COS by ESR. Details are not given. SO detected as product.	EX	297	(7.2±0.4)(9)			2	
73 SCH Suggested error limits of ± 35%.	SE	270-1500	4.1(13)		2556±70	2	
74 KLE/STI Flash photolysis - resonance fluorescence. O formed by flash photolysis of O_2; its decay was measured by resonance fluoresence in excess COS and 50 Torr He or 40-200 Torr Ar.	EX	263-503	(9.94±0.78)(12)		2166±28	2	
75 WEI/TIM Discharge flow. O formed by microwave discharge in O_2 or N_2 (followed by N+NO rn.) diluted with He, was monitored in excess COS by ESR. P=0.69-1.49 at 295 K.	EX	239-404	(1.2±0.2)(13)		2149±35	2	
76 BAU/DRY Estimated uncertainty is 50% below 600 K and a factor of 3 above 600 K.	SE	190-1200	1.6(13)		2250	2	
76 MAN/BRA Flash photolysis-resonance fluorescence. Photolysed mixtures of COS, O_2, Ar, and either CH_3F or CH_2F_2. Resonance fluorescence detection of O decay in excess COS. Rate was not significantly increased by vibrational excitation of COS.	EX	296	(8.37±0.84)(9)			2	

O + COS → products -- Continued

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
78 YOS/SAI Discharge flow. O formed by microwave discharge in O_2. Excess COS. Formation of SO monitored by microwave absorption. Ratio of consumption of O to formation of SO was found to be unity. P=0.13 Torr.	EX	297	(7.1±0.7)(9)			2	
79 HSU/SHA *) Vibrational distribution of CO product measured by CO laser resonance absorption method. Vibrational distribution was independent of the O isotope (16 or 18), indicating direct stripping of S by O (i.e., O in CO arises from COS).	EX		*)				
80 ROB/SMI Laser photolysis-chemiluminescence. O formed by laser photolysis of O_3 at 275nm. k was obtained by least squares fit of a reaction mechanism to the measured time dependence of the $SO+O_3$ chemiluminescence. $P(N_2)$=100 Torr.	EX	296	(1.0±0.1)(10)			2	
81 KRU/WAG	EX	1900	1.8(13)			2	
	DE	298-1900	7.5(13)	0	2754	2	
	DE	298-1900	7.4(12)	1.0	2057	2	
Shock tube. O generated by decomposition of N_2O in Ar and monitored by resonance absorption. The two alternative T-dependence expressions were derived by combining the data with other results in the literature (67 HOY/WAG and 68 HOM/KRO).							
84 BAU/COX	SE	298	8.4(9)			2	1.6
	SE	220-600	1.6(13)		2250±150	2	
For discussion see 80 BAU/COX. Note that only data for T<600 K are considered and that the data above 600 K are significantly higher than the fitted line.							
85 DEM/MAR	SE	298	7.8(9)			2	1.2
	SE		1.3(13)		2200±150	2	
Averaged the room temp. data of 69 WES/DEH, 74 KLE/STI, 75 WEI/TIM, 76 MAN/BRA, 72 BRE/MIL; averaged the B values of 69 WES/DEH, 74 KLE/STI, 75 WEI/TIM.							

O + COS → products -- Continued

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
Recommended value of k	RE	298	8.0(9)			2	1.2
Recommended values of Arrhenius A and B	RE	239-523	1.6(13)		2257±200	2	1.3
Recommended values of Arrhenius A and B	RE	239-1900	4.7(13)		2621±200	2	1.5

Based on least squares fitting of all data in the data sheet for (a) 239-523 and (b) 239-1900 K temp. ranges.

Arrhenius plot for O+COS→products is shown in Fig. 5. The insert in Fig. 5 shows an enlarged area (for greater clarity) with several additional k values (those reported at room temperature only).

References for reaction O + COS → products

65 ROL/REE Rolfes, T.R., Reeves, R.R., Jr., and Harteck, P., "The chemiluminescent reaction of oxygen atoms with sulfur monoxide at low pressures," J. Phys. Chem. 69, 849 (1965).

65 SUL/WAR Sullivan, J.O., and Warneck, P., "Mass spectrometric investigation of the reaction between oxygen atoms and carbonyl sulfide," Ber. Bunsenges. Phys. Chem. 69, 7 (1965).

67 HOY/WAG Hoyermann, K., Wagner, H.Gg., and Wolfrum, J., "Bestimmung der Geschwindigkeit der Reaktion O + COS → CO + SO," Ber. Bunsenges. Phys. Chem. 71, 603 (1967).

68 HOM/KRO Homann, K.H., Krome, G., and Wagner, H.Gg., "Schwefelkohlenstoff-oxydation, geschwindigkeit von elementarreaktionen. Teil 1," Ber. Bunsenges. Phys. Chem. 72, 998 (1968).

69 WES/DEH Westenberg, A.A., and deHaas, N., "Atom-molecule kinetics using ESR detection. V. Results for O + OCS, O + CS_2, O + NO_2, and H + C_2H_4," J. Chem. Phys. 50, 707 (1969).

71 KRE/SIM Krezenski, D.C., Simonaitis, R., and Heicklen, J., "The reactions of $O(^3P)$ with ozone and carbonyl sulfide," Int. J. Chem. Kinet. 3, 467 (1971).

72 BRE/MIL Breckenridge, W.H., and Miller, T.A., "Kinetic study by EPR of the production and decay of $SO(^1\Delta)$ in the reaction of O_2 $(^1\Delta_g)$ with $SO(^3\Sigma^-)$," J. Chem. Phys. 56, 465 (1972).

73 SCH Schofield, K., "Evaluated chemical kinetic rate constants for various gas phase reactions," J. Phys. Chem. Ref. Data 2, 25 (1973).

74 KLE/STI Klemm, R.B., and Stief, L.J., "Absolute rate parameters for the reaction of ground state atomic oxygen with carbonyl sulfide," J. Chem. Phys. 61, 4900 (1974).

75 WEI/TIM Wei, C.-N., and Timmons, R.B., "ESR study of the kinetics of the reactions of $O(^3P)$ atoms with CS_2 and OCS," J. Chem. Phys. 62, 3240 (1975).

76 BAU/DRY Baulch, D.L., Drysdale, D.D., Duxbury, J., and Grant, S.J., "Homogeneous gas phase reactions of the O_2-O_3 system, the CO-O_2-H_2 system, and of sulphur-containing species," in 'Evaluated Kinetic Data for High Temperature Reactions', Vol. 3, Butterworths, London (1976).

76 MAN/BRA Manning, R.G., Braun, W., and Kurylo, M.J., "The effect of infrared laser excitation on reaction dynamics: O + C_2H_4* and O + OCS*," J. Chem. Phys. 65, 2609 (1976).

78 YOS/SAI Yoshida, N., and Saito, S., "Application of microwave spectroscopy to kinetic study of the reaction of carbonyl sulfide with atomic oxygen," Bull. Chem. Soc. Japan 51, 1635 (1978).

References for reaction O + COS → products -- Continued

79 HSU/SHA Hsu, D.S.Y., Shaub, W.M., Burks, T.L, and Lin, M.C., "Dynamics of reactions of O(^{3}P) atoms with CS, CS_2, and OCS," Chem. Phys. 44, 143 (1979).

80 BAU/COX Baulch, D.L., Cox, R.A., Hampson, R.F., Jr., Kerr, J.A., Troe, J., and Watson, R.T., "Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry," J. Phys. Chem. Ref. Data 9, 295 (1980).

80 ROB/SMI Robertshaw, J. S., and Smith, I. W. M., "Rate data for O + OCS → SO + CO and SO + O_3 → SO_2 + O_2 by a new time-resolved technique," Int. J. Chem. Kinet. 12, 729 (1980).

81 KRU/WAG Kruger, B., and Wagner, H.Gg., "Shock tube study of the rate constant of the reaction of oxygen atoms with carbonyl sulfide," Z. Phys. Chem. Neue Folge 126, 1 (1981).

84 BAU/COX Baulch, D.L., Cox, R.A., Hampson, R.F., Jr., Kerr, J.A., Troe, J., and Watson, R.T., "Evaluated kinetic and photochemical data for atmospheric chemistry: supplement II," J. Phys. Chem. Ref. Data 13, 1259 (1984).

85 DEM/MAR NASA Panel for Data Evaluation: DeMore, W.B., Margitan, J.J., Molina, M.J., Watson, R.T., Golden, D.M., Hampson, R.F., Kurylo, M.J., Howard, C.J., and Ravishankara, A.R., "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling. Evaluation number 7," J.P.L. Publ. 85-37 (1985).

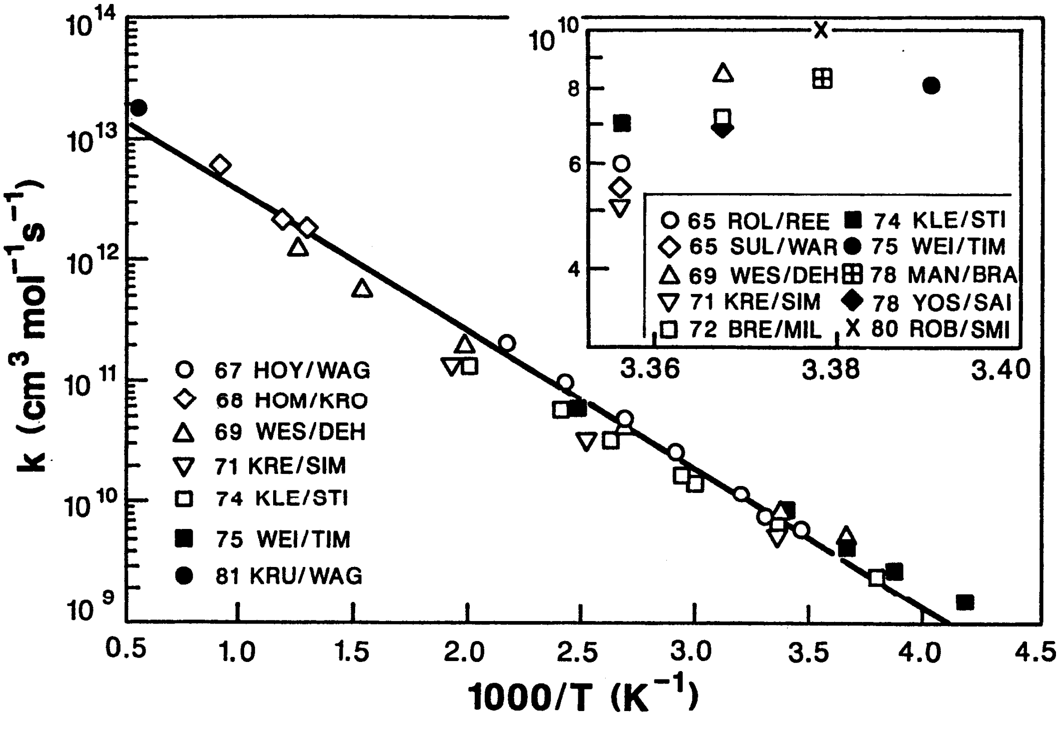

Fig. 5. Arrhenius plot for the reaction O+COS→products.
The line is calculated using the recommended A and B values at 239-1900K.

$O + COS \rightarrow CO_2 + S$

O + Carbon oxide sulfide

A higher temperature path in the rn. O + COS → products

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
82 TOP Shock tube oxidation of COS. Monitored COS, O_2, CO, CO_2, SO_2 and total pressure. The relative rates of CO_2 and CO production at the beginning of the COS conversion phase were interpreted to estimate k for the rn. path $O + COS \rightarrow CO_2 + S$.	EX	1200-1900	5.0(13)		5527±636	2	
Recommended value of k	RE	1200	5(11)			2	3
Recommended values of Arrhenius A and B	RE	1200-1900	5(13)		5530±1000	2	3
Based on the single determination (82 TOP). Additional data would be useful.							

Reference for reaction $O + COS \rightarrow CO_2 + S$

82 TOP Topaloglu, T., "A shock tube study of carbonyl sulfide oxidation," Diss. Abst. Int. B 42, 4134 (1982).

$O + CH_3SH \rightarrow$ products

O + Methanethiol

For potential rn. channels see 76 SLA/GRA, 78 KIR/VET, and 81 CVE/SIN.

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
76 SLA/GRA Discharge flow. Photoionization mass spec. Monitored decay of CH_3SH in excess O atoms. P= 0.64-2.0 Torr.	EX	300	1.1(12)			2	1.2
78 KIR/VET Discharge flow. High resolution mass spec. Monitored decay of thiol in excess O atoms. P=~1 Torr. Rate constant measurements at 302 K based on thiol decay agree with those based on O atom decay when thiol was in sufficient excess (100 fold), but were otherwise larger.	EX	300-661	(8.5±1.0)(12)		625±36	2	

$O + CH_3SH \rightarrow$ **products** -- Continued

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
78 SLA/BAI *) n=4.53±0.49 Discharge flow. Photoionization mass spec. Monitored decay of CH_3SH in excess O atoms. P= 0.745-2.25 Torr. [A, n, and B values were calculated (87 SIN/CVE) from the supplementary data of 78 SLA BAI].	EX	252-496	(2.65±1.52)(10)	*)	-1135±169	2	
81 NIP/SIN *) n=3.65±0.61. P=22-61 Torr. Phase shift technique with modulated [O] monitored by O+NO chemiluminescence. O atoms generated by Hg-photosensitized decomposition of N_2O. 81 NIP/SIN report the rate expression k = (9.16±1.02)(11) + (3.85±2.41)(13)x exp(-(1673±322)/T). [A, n, and B values listed here were calculated (87 SIN/CVE) from the data of 81 NIP/SIN].	EX	297-537	(6.58±5.05)(10)	*)	-829±234	2	
Recommended value of k	RE	298	1.2(12)			2	1.2
Recommended values of Arrhenius parameters	RE	252-661	*)	*)	*)	2	1.3

*) Strongly curved Arrhenius plot: fitted all data to k=A1+A2exp(-B/T) with A1=9.0(11), A2=1.8(13), B=1261. Although the agreement between the reported studies is reasonable, they differ in finer details. The Arrhenius plot is reported to be curved according to 78 SLA/BAI and 81 NIP/SIN, although the data of 78 SLA/BAI are consistently about 15% higher than those of 81 NIP/SIN. However, there was no evidence in 78 KIR/VET of an Arrhenius plot curvature in the same temp. interval.
The present recommended Arrhenius parameters, A1, A2 and B, have been obtained by a least squares fit of all data in the data sheet to the composite Arrhenius expression. The data of 81 NIP/SIN fall below the fitted line; for example the fitted k(298) value is 1.17(12), which is about 10% greater than the value 1.06(12) of 81 NIP/SIN.

Arrhenius plot for $O+CH_3SH \rightarrow$products is shown in Fig. 6.

References for reaction $O + CH_3SH \rightarrow$ products

76 SLA/GRA	Slagle, I.R., Graham, R.E., and Gutman, D., "Direct identification of reactive routes and measurement of rate constants in the reacions of oxygen atoms with methanethiol, ethanethiol, and methylsulfide," Int. J. Chem. Kinet. **8**, 451 (1976).
78 KIR/VET	Kirchner, K., Vettermann, R., and Indruch, H., "Kinetics of the reactions of mercaptans with $O(^3P)$ under consideration of the influence of molecular oxygen," Ber. Bunsenges. Phys. Chem. **82**, 1223 (1978).
78 SLA/BAI	Slagle, I.R., Baiocchi, F., and Gutman, D., "Study of the reactions of oxygen atoms with hydrogen sulfide, methanethiol, ethanethiol, and methyl sulfide," J. Phys. Chem. **82**, 1333 (1978).

References for reaction O + CH_3SH → products -- Continued

81 CVE/SIN Cvetanovic, R.J., Singleton, D.L., and Irwin, R.S, "Gas-Phase Reactions of O(^{3}P) Atoms with Methanethiol, Ethanethiol, Methyl Sulfide, and Dimethyl Disulfide. 2. Reaction Products and Mechanisms," J. Am. Chem. Soc. 103, 3530 (1981).

81 NIP/SIN Nip, W.S., Singleton, D.L., and Cvetanovic, R.J., "Gas-phase reactions of O(^{3}P) atoms with methanethiol, ethanethiol, methyl sulfide, and dimethyl disulfide. 1. Rate constants and Arrhenius parameters," J. Am. Chem. Soc. 103, 3526 (1981).

87 SIN/CVE Singleton, D.L., and Cvetanovic, R.J., The present evaluation.

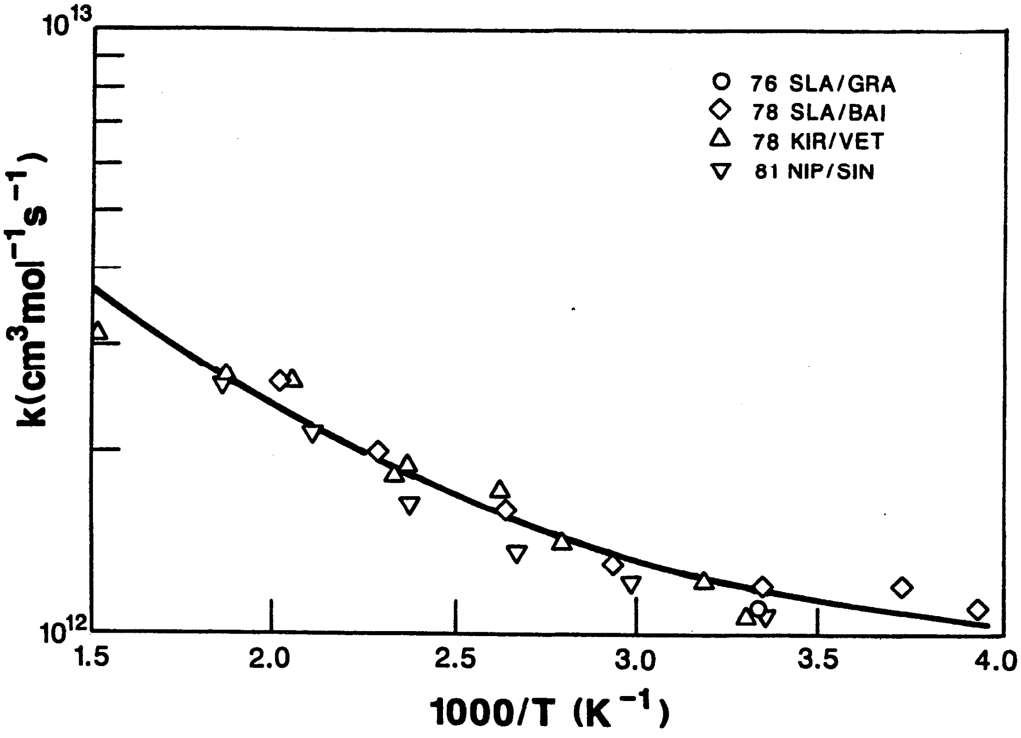

Fig. 6. Arrhenius plot for the reaction O+CH_3SH→products.
The line is calculated using the modified Arrhenius Eqn. k=A1+A2exp(-B/T) and the recommended values: A1=9.0(11)cm^{3}mol^{-1}s^{-1}, A2=1.8(13)cm^{3}mol^{-1}s^{-1}, B=1261K.

O + C_2H_5SH → products

O + Ethanethiol

For potential rn. channels see 76 SLA/GRA, 78 KIR/VET, and 81 CVE/SIN.

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
76 SLA/GRA Discharge flow. Photoionization mass spec. Monitored decay of C_2H_5SH in excess O atoms. P= 0.64-2.0 Torr.	EX	300	1.7(12)			2	1.2

O + C_2H_5SH → products -- Continued

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
78 KIR/VET Discharge flow. High resolution mass spec. Monitored decay of thiol in excess O atoms. P=~1 Torr. Rate constant measurements at 302 K based on thiol decay agree with those based on O atom decay when thiol was in sufficient excess (100 fold), but were otherwise larger.	EX	304-421	(5.75±0.3)(12)		391±18	2	
78 SLA/BAI *) n=6.13±1.04 Discharge flow. Photoionization mass spec. Monitored decay of C_2H_5SH in excess O atoms. P= 0.719-2.16 Torr. [A, n, and B values were calculated (87 SIN/CVE) from the supplementary data of 78 SLA BAI].	EX	256-496	(3.17±3.84)(9)	*)	-1882±356	2	
81 NIP/SIN *) n=4.66±0.31. P=21-50 Torr. Phase shift technique with modulated [O] monitored by O+NO chemiluminescence. O atoms generated by Hg-photosensitized decomposition of N_2O. 81 NIP/SIN report the rate expression k = (1.37±0.66)(12) + (8.73±4.46)(13)x exp(-(2075±268)/T). [A, n, and B values listed here were calculated (87 SIN/CVE) from the data of 81 NIP/SIN].	EX	300-574	(1.78±0.71)(10)	*)	-1313±122	2	
Recommended value of k	RE	298	1.7(12)			2	1.2
Recommended values of Arrhenius parameters	RE	256-574	*)	*)	*)	2	1.4

*) Strongly curved Arrhenius plot: fitted all data to k=A1+A2exp(-B/T) with A1=1.6(12), A2=1.0(14), B=2198. As for O+CH_3SH, the reported data are in reasonable agreement, although they differ in finer details. A curved Arrhenius plot is reported in 78 SLA/BAI and 81 NIP/SIN, although the value of 78 SLA/BAI is as much as 20% greater than that of 81 NIP/SIN at room temp. However, there was no evidence of an Arrhenius plot curvature in 78 KIR/VET.

The present recommended Arrhenius parameters, A1, A2 and B, have been obtained by a least squares fit of all data in the data sheet to the composite Arrhenius expression. The data of 81 NIP/SIN lie below the fitted line; for example the fitted k(298) value is 1.70(12), which is about 15% greater than the value 1.47(12) of 81 NIP/SIN.

Arrhenius plot for O+C_2H_5SH→products is shown in Fig. 7.

References for reaction O + $C_2H_5SH \rightarrow$ products

76 SLA/GRA Slagle, I.R., Graham, R.E., and Gutman, D., "Direct identification of reactive routes and measurement of rate constants in the reacions of oxygen atoms with methanethiol, ethanethiol, and methylsulfide," Int. J. Chem. Kinet. 8, 451 (1976).

78 KIR/VET Kirchner, K., Vettermann, R., and Indruch, H., "Kinetics of the reactions of mercaptans with $O(^3P)$ under consideration of the influence of molecular oxygen," Ber. Bunsenges. Phys. Chem. 82, 1223 (1978).

78 SLA/BAI Slagle, I.R., Baiocchi, F., and Gutman, D., "Study of the reactions of oxygen atoms with hydrogen sulfide, methanethiol, ethanethiol, and methyl sulfide," J. Phys. Chem. 82, 1333 (1978).

81 CVE/SIN Cvetanovic, R.J., Singleton, D.L., and Irwin, R.S, "Gas-Phase Reactions of $O(^3P)$ Atoms with Methanethiol, Ethanethiol, Methyl Sulfide, and Dimethyl Disulfide. 2. Reaction Products and Mechanisms," J. Am. Chem. Soc. 103, 3530 (1981).

81 NIP/SIN Nip, W.S., Singleton, D.L., and Cvetanovic, R.J., "Gas-Phase Reactions of $O(^3P)$ Atoms with Methanethiol, Ethanethiol, Methyl Sulfide, and Dimethyl Disulfide. 1. Rate Constants and Arrhenius Parameters," J. Am. Chem. Soc. 103, 3526 (1981).

87 SIN/CVE Singleton, D.L., and Cvetanovic, R.J., The present evaluation.

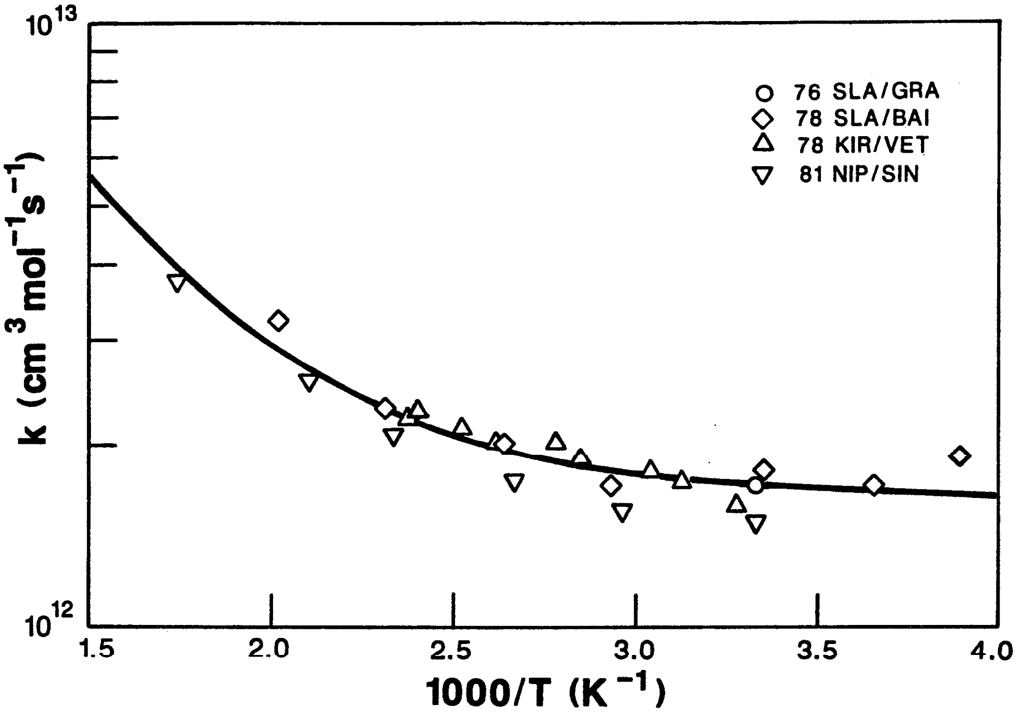

Fig. 7. Arrhenius plot for the reaction O+$C_2H_5SH \rightarrow$products.
The line is calculated using the modified Arrhenius Eqn. k=A1+A2exp(-B/T) and the recommended values: A1=1.6(12)cm^{3}mol^{-1}s^{-1}, A2=1.0(14)cm^{3}mol^{-1}s^{-1}, B=2198K.

O + C_3H_7SH → products

O + 1-Propanethiol

For potential rn. channels see 76 SLA/GRA, 78 KIR/VET, and 81 CVE/SIN.

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
78 KIR/VET Discharge flow. High resolution mass spec. Monitored decay of thiol in excess O atoms. P=~1 Torr.	EX	303-421	(8.33±0.54)(12)		494±22	2	
Recommended value of k	RE	298	1.6(12)			2	1.3
Recommended values of Arrhenius A and B	RE	303-421	8.3(12)		494±50	2	1.5
Based on the only data available (78 KIR/VET). Additional determinations would be useful.							

References for reaction O + C_3H_7SH → products

76 SLA/GRA	Slagle, I.R., Graham, R.E., and Gutman, D., "Direct identification of reactive routes and measurement of rate constants in the reacions of oxygen atoms with methanethiol, ethanethiol, and methylsulfide," Int. J. Chem. Kinet. 8, 451 (1976).
78 KIR/VET	Kirchner, K., Vettermann, R., and Indruch, H., "Kinetics of the reactions of mercaptans with O(^{3}P) under consideration of the influence of molecular oxygen," Ber. Bunsenges. Phys. Chem. 82, 1223 (1978).
81 CVE/SIN	Cvetanovic, R.J., Singleton, D.L., and Irwin, R.S, "Gas-Phase Reactions of O(^{3}P) Atoms with Methanethiol, Ethanethiol, Methyl Sulfide, and Dimethyl Disulfide. 2. Reaction Products and Mechanisms," J. Am. Chem. Soc. 103, 3530 (1981).

O + C_4H_9SH → products

O + 1-Butanethiol

For potential rn. channels see 76 SLA/GRA, 78 KIR/VET, and 81 CVE/SIN.

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
78 KIR/VET Discharge flow. High resolution mass spec. Monitored decay of thiol in excess O atoms. P=~1 Torr.	EX	306-419	(5.78±0.33)(12)		321±19	2	
Recommended value of k	RE	298	2.0(12)			2	1.3
Recommended values of Arrhenius A and B	RE	306-419	5.8(12)		321±50	2	1.5
Based on the only data available (78 KIR/VET). Additional determinations would be useful.							

References for reaction O + C_4H_9SH → products

76 SLA/GRA Slagle, I.R., Graham, R.E., and Gutman, D., "Direct identification of reactive routes and measurement of rate constants in the reacions of oxygen atoms with methanethiol, ethanethiol, and methylsulfide," Int. J. Chem. Kinet. 8, 451 (1976).

78 KIR/VET Kirchner, K., Vettermann, R., and Indruch, H., "Kinetics of the reactions of mercaptans with O(^{3}P) under consideration of the influence of molecular oxygen," Ber. Bunsenges. Phys. Chem. 82, 1223 (1978).

81 CVE/SIN Cvetanovic, R.J., Singleton, D.L., and Irwin, R.S, "Gas-Phase Reactions of O(^{3}P) Atoms with Methanethiol, Ethanethiol, Methyl Sulfide, and Dimethyl Disulfide. 2. Reaction Products and Mechanisms," J. Am. Chem. Soc. 103, 3530 (1981).

O + $C_5H_{11}SH$ → products

O + 1-Pentanethiol

For potential rn. channels see 76 SLA/GRA, 78 KIR/VET, and 81 CVE/SIN.

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
78 KIR/VET Discharge flow. High resolution mass spec. Monitored decay of thiol in excess O atoms. P=~1 Torr.	EX	302-409	(6.18±0.35)(12)		328±19	2	
Recommended value of k	RE	298	2.1(12)			2	1.3
Recommended values of Arrhenius A and B	RE	302-409	6.2(12)		328±50	2	1.5
Based on the only data available (78 KIR/VET). Additional determinations would be useful.							

References for reaction O + $C_5H_{11}SH$ → products

76 SLA/GRA Slagle, I.R., Graham, R.E., and Gutman, D., "Direct identification of reactive routes and measurement of rate constants in the reacions of oxygen atoms with methanethiol, ethanethiol, and methylsulfide," Int. J. Chem. Kinet. 8, 451 (1976).

78 KIR/VET Kirchner, K., Vettermann, R., and Indruch, H., "Kinetics of the reactions of mercaptans with O(^{3}P) under consideration of the influence of molecular oxygen," Ber. Bunsenges. Phys. Chem. 82, 1223 (1978).

81 CVE/SIN Cvetanovic, R.J., Singleton, D.L., and Irwin, R.S, "Gas-Phase Reactions of O(^{3}P) Atoms with Methanethiol, Ethanethiol, Methyl Sulfide, and Dimethyl Disulfide. 2. Reaction Products and Mechanisms," J. Am. Chem. Soc. 103, 3530 (1981).

$O + CH_3SCH_3 \rightarrow$ products

O + Methane, thiobis-

Presumably $O + CH_3SCH_3 \rightarrow CH_3SO + CH_3$. For potential rn. channels see 76 SLA/GRA, 78 KIR/VET, and 81 CVE/SIN.

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
74 CAD/WIC Discharge flow. Excess CH_3SCH_3. [O] monitored by O+NO chemiluminenscence.	EX	300	3.3(11)			2	
76 LEE/TIM Flash photolysis. [O] monitored by resonance fluorescence in excess CH_3SCH_3. O_2 used as source of O atoms. P=40-100 Torr (Ar).	EX	268-424	(8.56±0.42)(12)		-366±16	2	
76 SLA/GRA Discharge flow. Photoionization mass spec. Monitored decay of CH_3SCH_3 in excess O atoms. P= 0.6-1.9 Torr.	EX	300	3.8(13)			2	1.2
78 SLA/BAI Discharge flow. Photoionization mass spec. Monitored decay of CH_3SCH_3 in excess O atoms. P= 0.7-1.2 Torr. [A and B values were calculated (87 SIN/CVE) from the supplementary data of 78 SLA/BAI].	EX	252-493	(1.16±0.08)(13)		-300±22	2	
80 LEE/TAN1 Discharge flow. [O] monitored by resonance fluorescence in excess sulfide. P = 1.1-2.8 Torr.	EX	272-472	(7.71±0.72)(12)		-404±30	2	
81 NIP/SIN Phase shift technique with modulated [O] monitored by O+NO chemiluminescence. O atoms generated by Hg-photosensitized decomposition of N_2O. P=22-56 Torr at 297 K.	EX	296-557	(6.69±0.72)(12)		-460±41	2	
81 NIP/SIN	RL	300	13.8±0.9			2/2	
Reference rn. $O + 1\text{-Butene} \rightarrow$ products O formed by Hg-photosensitized decomposition of N_2O. Monitored the rate of formation of butene oxide and n-butanal as a function of the ratio of reactants. The above RN k value was calculated (81 NIP/SIN) using $k_{ref}=2.42(12)$ $cm^3 mole^{-1} s^{-1}$.	RN	300	(3.32±0.25)(13)			2	

$O + CH_3SCH_3 \rightarrow$ products -- Continued

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
84 BAU/COX	SE	298	3.0(13)			2	1.25
	SE	270-560	7.8(12)		-409±100	2	
Fitted by least squares the data of 76 LEE/TIM, 80 LEE/TAN, 81 NIP/SIN, and excluded the data of 76 SLA/GRA, 78 SLA/BAI.							
Recommended value of k	RE	298	3.1(13)			2	1.2
Recommended values of Arrhenius A and B	RE	252-557	8.2(12)		-397±100	2	1.3

Assigned zero weight to the very low k of 74 CAD/WIC. (If the treatment is restricted to the same data as used in 84 BAU/COX and 74 CAD/WIC is excluded, the values would be only slightly altered: for T=268-557 K k(298)=3.0(13), A=7.4(12), B=-416±100, and k err. factor=1.3).

Arrhenius plots for the reaction $O+CH_3SCH_3 \rightarrow$ products are shown in Fig. 8.

References for reaction $O + CH_3SCH_3 \rightarrow$ products

74 CAD/WIC	Cadle, R.D., Wickman, H.H., Hall, C.B., and Eberle, K.M., "The reaction of atomic oxygen with formaldehyde, crotonaldehyde, and dimethyl sulfide," Chemosphere 3, 115 (1974).
76 LEE/TIM	Lee, J.H., Timmons, R.B., and Stief, L.J., "Absolute rate parameters for the reaction of ground state atomic oxygen with dimethyl sulfide and episulfide," J. Chem. Phys. 64, 300 (1976).
76 SLA/GRA	Slagle, I.R., Graham, R.E., and Gutman, D., "Direct identification of reactive routes and measurement of rate constants in the reacions of oxygen atoms with methanethiol, ethanethiol, and methylsulfide," Int. J. Chem. Kinet. 8, 451 (1976).
78 KIR/VET	Kirchner, K., Vettermann, R., and Indruch, H., "Kinetics of the reactions of mercaptans with $O(^3P)$ under consideration of the influence of molecular oxygen," Ber. Bunsenges. Phys. Chem. 82, 1223 (1978).
78 SLA/BAI	Slagle, I.R., Baiocchi, F., and Gutman, D., "Study of the reactions of oxygen atoms with hydrogen sulfide, methanethiol, ethanethiol, and methyl sulfide," J. Phys. Chem. 82, 1333 (1978).
80 LEE/TAN1	Lee, J.H., Tang, I.N., and Klemm, R.B., "Absolute rate constant for the reaction of $O(^3P)$ with CH_3SCH_3 from 272 to 472K," J. Chem. Phys. 72, 1793 (1980).
81 CVE/SIN	Cvetanovic, R.J., Singleton, D.L., and Irwin, R.S, "Gas-Phase Reactions of $O(^3P)$ Atoms with Methanethiol, Ethanethiol, Methyl Sulfide, and Dimethyl Disulfide. 2. Reaction Products and Mechanisms," J. Am. Chem. Soc. 103, 3530 (1981).
81 NIP/SIN	Nip, W.S., Singleton, D.L., and Cvetanovic, R.J., "Gas-Phase Reactions of $O(^3P)$ Atoms with Methanethiol, Ethanethiol, Methyl Sulfide, and Dimethyl Disulfide. 1. Rate Constants and Arrhenius Parameters," J. Am. Chem. Soc. 103, 3526 (1981).
84 BAU/COX	Baulch, D.L., Cox, R.A., Hampson, R.F., Jr., Kerr, J.A., Troe, J., and Watson, R.T., "Evaluated kinetic and photochemical data for atmospheric chemistry: supplement II," J. Phys. Chem. Ref. Data 13, 1259 (1984).
87 SIN/CVE	Singleton, D.L., and Cvetanovic, R.J., The present evaluation.

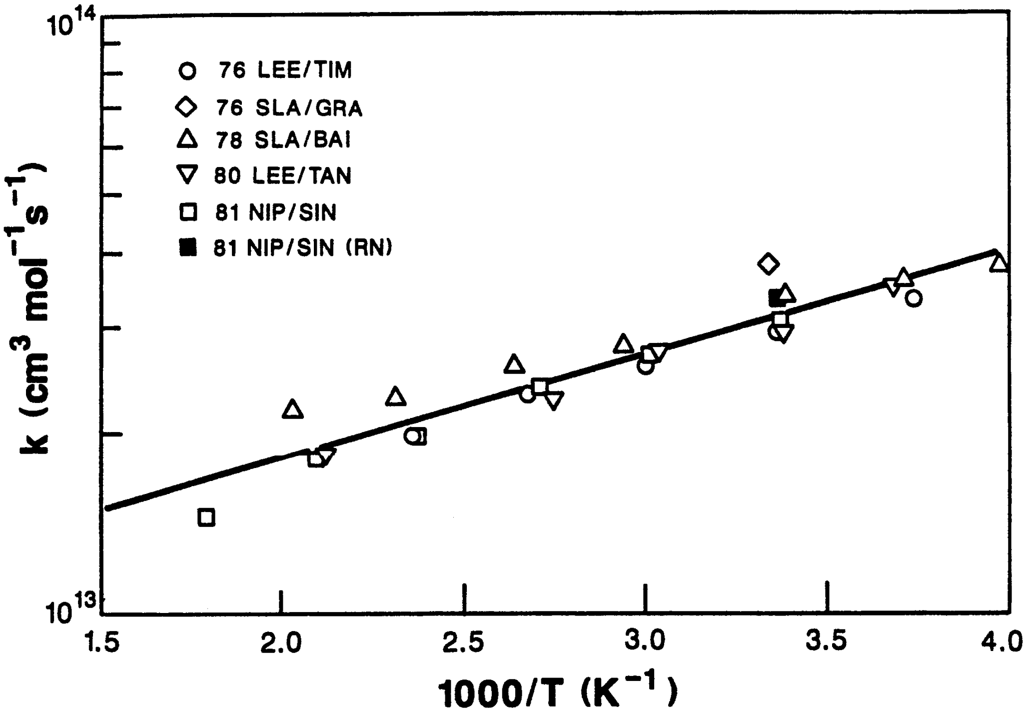

Fig. 8. Arrhenius plots for the reaction $O + CH_3SCH_3 \rightarrow$ products.
The line is calculated using the recommended A and B values.

$O + cy\text{-}CH_2SCH_2 \rightarrow$ products

<u>O + Ethylene episulfide</u>

The exclusive primary products appear to be $CH_2=CH_2$ + SO (76 LEE/TIM, 87 SIN).

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
76 LEE/TIM Flash photolysis. [O] monitored by resonance fluorescence in excess cy-CH_2SCH_2. O_2 used as source of O atoms. P=40-100 Torr (Ar).	EX	268-424	(8.07±0.54)(12)		18±20	2	
Recommended value of k	RE	298	7.6(12)			2	1.3
Recommended values of Arrhenius A and B Based on the only data available (76 LEE/TIM). Additional determinations would be useful.	RE	268-424	8.1(12)		18±50	2	1.5

References for reaction $O + cy\text{-}CH_2SCH_2 \rightarrow$ products

76 LEE/TIM Lee, J.H., Timmons, R.B., and Stief, L.J., "Absolute rate parameters for the reaction of ground state atomic oxygen with dimethyl sulfide and episulfide," J. Chem. Phys. 64, 300 (1976).

87 SIN Singleton, D.L., Unpublished data.

O + cy-CHCHSCHCH → products

O + Thiophene

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
81 LEE/TAN Discharge flow. O formed by microwave discharge of O_2 in He, followed by resonance fluorescence in excess thiophene. Abrupt change in the sign of the slope of the Arrhenius plot at ~ 260 K suggested to be possibly due to O addition at two different sites in thiophene (C=C and S).	EX	262-448	(2.01±0.20)(13)		569±30	2	
85 TAB/URE Discharge flow. O formed by microwave discharge in N_2O and Ar. The intensity of emission from excited SO_2 was determined at fixed reaction time for various initial excess thiophene concentrations. P < 2 Torr.	EX	379-525	(1.6±0.2)(12)		121	2	

Recommendation is not warranted: 81 LEE/TAN's data show a minimum at about 262 K and indicate a substantial positive activation energy at higher T (262-448 K). 85 TAB/URE, who only report data at higher temp. (379-525K), find essentially no temperature dependence, and their values are only 1/4 of the values at 425 K of 81 LEE/TAN. There appears a discrepancy in 85 TAB/URE between the reported Arrhenius expression and the data points plotted in their Figure 4 (the only place where rate constants at specific temperatures are presented). Additional determinations are needed.

Arrhenius plot for O+cy-CHCHSCHCH→products is shown in Fig. 9.

References for reaction O + cy-CHCHSCHCH → products

81 LEE/TAN Lee, J.H., and Tang, I.N., "Absolute rate constant for the reaction of O(^{3}P) with thiophene from 238 to 448K," J. Chem. Phys. 75, 137 (1981).

85 TAB/URE Tabares, F.L., and Urena, A.G., "Chemiluminescence and kinetic studies in O(^{3}P) + thiophene, pyrrole and furan mixtures," J. Chem. Soc. Faraday Trans. 2 81, 1395 (1985).

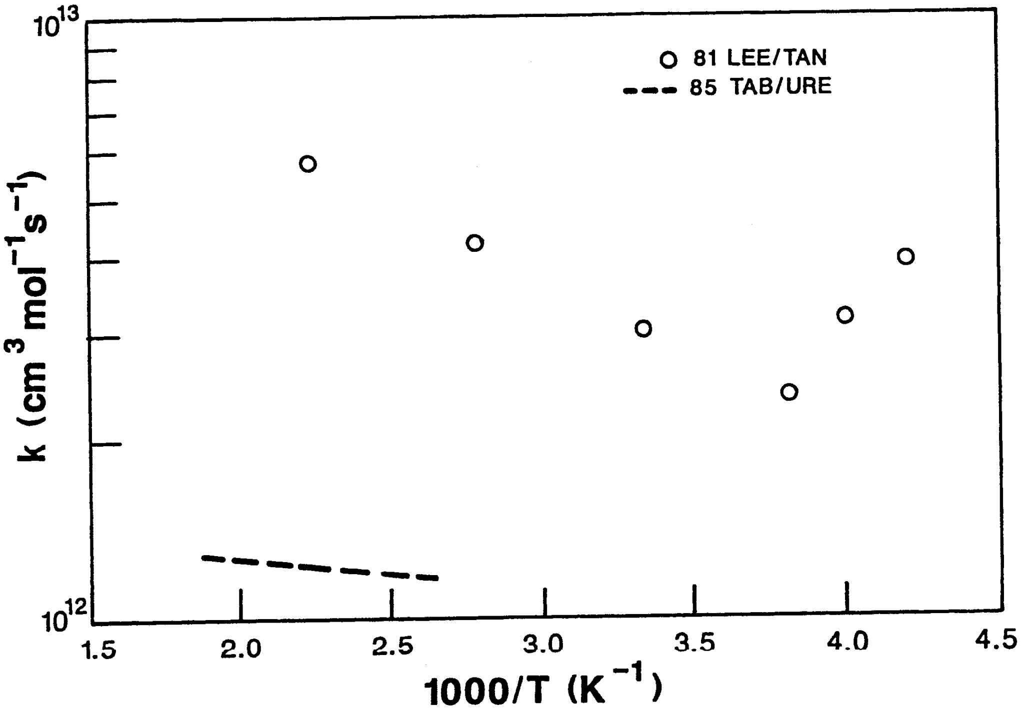

Fig. 9. Arrhenius plots for the reaction O+cy-CHCHSCHCH→products.

O + CH_3SSCH_3 → products

O + Disulfide, dimethyl-

For potential reaction channels see 81 CVE/SIN and 83 SIN/IRW.

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
80 LEE/TAN2 Discharge flow. [O] monitored by resonance fluorescence in excess sulfide. P=0.52-2.60 Torr.	EX	270-329	(1.28±0.13)(14)		0	2	
81 NIP/SIN Phase shift technique with modulated [O] monitored by O+NO chemiluminescence. O atoms formed by Hg-photosensitized decomposition of N_2O.	EX	298-571	(2.62±0.42)(13)		-251±61	2	

O + CH_3SSCH_3 → products -- Continued

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
81 NIP/SIN	RL	300	24.5±1.5			2/2	
	RN	300	(5.91±0.37)(13)			2	
Reference rn. O + 1-Butene → products O formed by Hg-photosensitized decomposition of N_2O. Monitored the rate of formation of butene oxide and n-butanal as a function of the ratio of reactants. The above RN k value was calculated (81 NIP/SIN) using k_{ref}=2.42(12) $cm^3 mole^{-1} s^{-1}$.							
84 BAU/COX	SE	298	7.8(13)			2	2
	SE	290-570	3.3(13)		-250±100	2	
Averaged the room temp. data of 80 LEE/TAN and 81 NIP/SIN, although they differ by a factor of 2. Accepted the B value of 81 NIP/SIN and adjusted A to give the k(298) value.							
Recommended value of k	RE	298	6.0(13)			2	1.2
Recommended values of Arrhenius A and B	RE	298-570	2.6(13)		-250±100	2	1.5

Based on the data of 81 NIP/SIN and assuming linear Arrhenius plot.

Arrhenius plot for O+CH_3SSCH_3→products is shown in Fig. 10.

References for reaction O + CH_3SSCH_3 → products

80 LEE/TAN2 Lee, J.H., and Tang, I.N., "Absolute rate constant for the reaction of O(^3P) with CH_3SSCH_3 from 270 to 329K," J. Chem. Phys. 72, 5718 (1980).

81 CVE/SIN Cvetanovic, R.J., Singleton, D.L., and Irwin, R.S, "Gas-Phase Reactions of O(^3P) Atoms with Methanethiol, Ethanethiol, Methyl Sulfide, and Dimethyl Disulfide. 2. Reaction Products and Mechanisms," J. Am. Chem. Soc. 103, 3530 (1981).

81 NIP/SIN Nip, W.S., Singleton, D.L., and Cvetanovic, R.J., "Gas-Phase Reactions of O(^3P) Atoms with Methanethiol, Ethanethiol, Methyl Sulfide, and Dimethyl Disulfide. 1. Rate Constants and Arrhenius Parameters," J. Am. Chem. Soc. 103, 3526 (1981).

83 SIN/IRW Singleton, D.L., Irwin, R.S., and Cvetanovic, R.J., "Mechanism of the reaction of oxygen atoms, O(^3P) with dimethyl disulfide," Can. J. Chem. 61, 968 (1983).

84 BAU/COX Baulch, D.L., Cox, R.A., Hampson, R.F., Jr., Kerr, J.A., Troe, J., and Watson, R.T., "Evaluated kinetic and photochemical data for atmospheric chemistry: supplement II," J. Phys. Chem. Ref. Data 13, 1259 (1984).

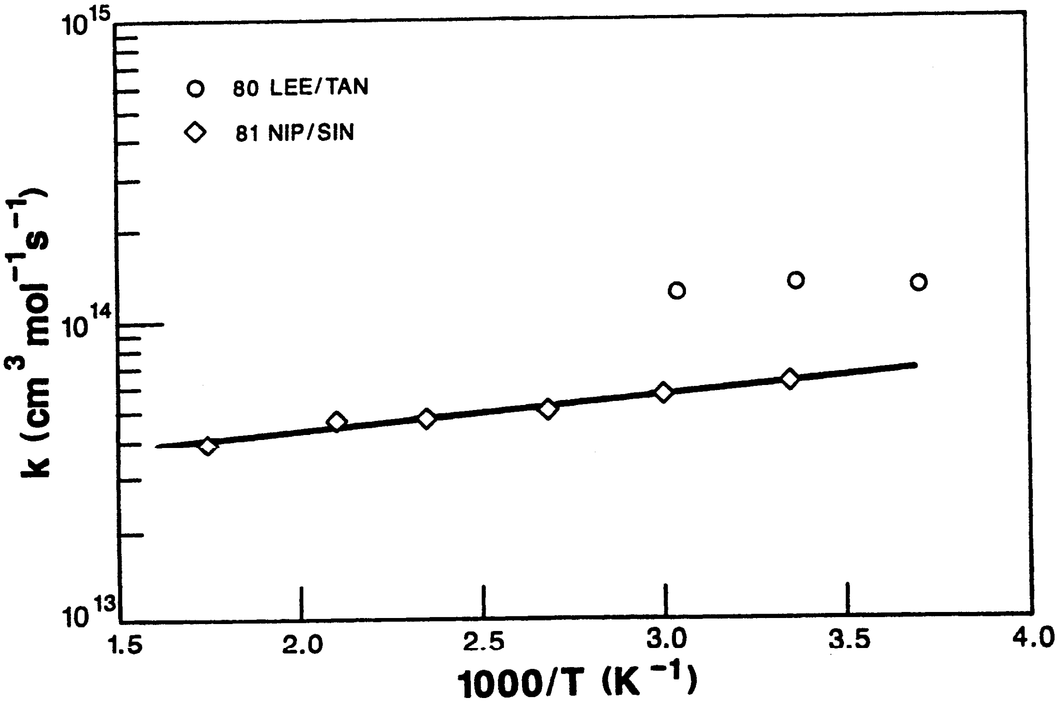

Fig. 10. Arrhenius plot for the O+CH_3SSCH_3→products reaction. The line is calculated using the recommended A and B values.

O + SCF_2 → products

O + Carbonothioic difluoride

Reference Code. Notes	Data type	T/K	k.k/k(ref). A,A/A(ref)	n	B, B-B(ref)	k.A units	k err. factor
79 SLA/GUT Discharge flow. O formed by microwave discharge of O_2 in He. Decay of SCF_2 in excess O measured by mass spec. P = 0.7-2.1 Torr at 298 K. Products identified in cross jet reactor indicated only the channel forming SO + CF_2.	EX	259-493	(7.35±1.1)(12)		376±48	2	
Recommended value of k	RE	298	2.1(12)			2	1.5
Recommended values of Arrhenius A and B	RE	259-493	7.4(12)		376±100	2	1.5
Based on the only data available (79 SLA/GUT). Additional determinations would be useful.							

Reference for reaction O + SCF_2 → products

79 SLA/GUT	Slagle, I.R., and Gutman, D., "Study of the reactions of oxygen atoms with carbonothioicdichloride, carbonothioicdifluoride, and tetrafluoro-1,3-dithietane," Int. J. Chem. Kinet. 11, 453 (1979).

O + $SCCl_2$ → products

<u>O + Carbonothioic dichloride</u>

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
79 SLA/GUT Discharge flow. O formed by microwave discharge of O_2 in He. Decay of $SCCl_2$ in excess O measured by mass spec. P = 0.7-2.1 Torr at 298 K. Products identified in cross jet reactor indicated two channels: $SO+CCl_2$ and $SCCl+ClO$.	EX	251-493	(1.86±0.33)(13)		-58±53	2	
Recommended value of k	RE	298	2.3(13)			2	1.3
Recommended values of Arrhenius A and B	RE	251-493	1.9(13)		-60±100	2	1.5
Based on the only data available (79 SLA/GUT). Additional determinations would be useful.							

Reference for reaction O + $SCCl_2$ → products

79 SLA/GUT	Slagle, I.R., and Gutman, D., "Study of the reactions of oxygen atoms with carbonothioicdichloride, carbonothioicdifluoride, and tetrafluoro-1,3-dithietane," Int. J. Chem. Kinet. 11, 453 (1979).

O + cy-CF_2SCF_2S → products

<u>O + 1,3-dithietane, 2,2,4,4-tetrafluoro-</u>

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
79 SLA/GUT Discharge flow. O formed by microwave discharge of O_2 in He. Monitored decay of cy-CF_2SCF_2S in excess O by mass spec. P=0.7-2.1 Torr at 298 K. Products identified in cross jet reactor indicated only the channel forming $SO+CF_2+SCF_2$.	EX	253-493	(1.42±0.31)(13)		855±64	2	

O + cy-CF_2SCF_2S → products -- Continued

Reference Code, Notes	Data type	T/K	k,k/k(ref), A,A/A(ref)	n	B, B-B(ref)	k,A units	k err. factor
Recommended value of k	RE	298	8.1(11)			2	1.3
Recommended values of Arrhenius A and B	RE	253-493	1.4(13)		855±100	2	1.5
Based on the only data available (79 SLA/GUT). Additional determinations would be useful.							

Reference for reaction O + cy-CF_2SCF_2S → products

79 SLA/GUT Slagle, I.R., and Gutman, D., "Study of the reactions of oxygen atoms with carbonothioicdichloride, carbonothioicdifluoride, and tetrafluoro-1,3-dithietane," Int. J. Chem. Kinet. **11**, 453 (1979).