NIST–JANAF Thermochemical Tables for the Bromine Oxides

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The thermodynamic and spectroscopic properties of the bromine oxide species have been reviewed. Recommended NIST-JANAF Thermochemical Tables are given for six gaseous bromine oxides: BrO, OBrO, BrOO, BrOBr, BrBrO, and BrO₃. Sufficient information is not available to generate thermochemical tables for any condensed phase species. Annotated bibliographies (over 280 references) are provided for all neutral bromine oxides which have been reported in the literature. There are needs for additional experimental and theoretical data to reduce the uncertainties in the recommended values for these six species. Of all the species mentioned in the literature, many have not been isolated and characterized. In fact some do not exist. Throughout this paper, uncertainties attached to recommended values correspond to the uncertainty interval, equal to twice the standard deviation of the mean. © 1996 American Institute of Physics and American Chemical Society.

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

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1. Introduction

As a continuation of previous studies which dealt with the thermodynamic properties of the chlorine oxides¹ and oxygen fluorides,² this study deals with the neutral bromine oxides. A succeeding article will deal with iodine oxides. We will not discuss the astatine oxides, as there appears to be only an estimated D_0° value reported in the literature for AtO(g). Specifically, this study examines the thermodynamic properties of the neutral oxides, not the gaseous ionic and aqueous ionic species. The main purpose of this article is to

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

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

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

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

The current version (1985) of the JANAF Thermochemical Tables³ does not include any bromine oxygen species, whereas the 1989 version of the Thermophysical Properties of Individual Substances⁴ only includes BrO(g), for which 14 references are given: the latest of these being dated 1975. This latter critical review referred to data from four spectroscopic studies, two microwave studies, three EPR studies, four dissociation energy studies, and two earlier reviews. There are sufficient new data available to warrant a revision to this tabulation. The NBS Thermodynamic Tables⁵ and its Russian counterpart by Glushko and Medvedev⁶ listed values $(C_p^\circ, H^\circ, S^\circ, \text{ and } \Delta_f H^\circ)$ at 298.15 K for BrO(g), but only an enthalpy of formation for BrO₂(cr). [The NBS Tables also listed values for three aqueous ions, Glushko and Medvedev listed two aqueous ions.] It should be noted that the NBS study was performed in 1964 and the Russian study in 1965, and were based on the same references.

There are many NASA-JPL publications on chemical kinetics in which enthalpy of formation tables are given. Of all the bromine oxides, only BrO(g) is listed by NASA-JPL.⁷ These data are presented without citation or reference to the original source. Most of the recommendations are based upon data in the IUPAC Evaluation (Atkinson *et al.*, 1989,⁸ 1992⁹). Some of the values are different from the current IUPAC recommendations, reflecting recent studies that have not yet been accepted and incorporated into that publication. IUPAC cites the origin of their values. All citations given by IUPAC are included in this article.

Lewis¹⁰ in 1932 reviewed the kinetics of reactions that proceeded with velocities ranging from the flammable region to detonation. As part of this review the author summarized the kinetics of the explosion of ozone as sensitized by bromine. Lewis raised the question as to the possible formation of bromine oxides.

In a 1963 review article, Schmeisser and Brandle¹¹ summarized the data pertaining to the properties and chemistry of the halogen-oxide compounds. Although these authors did not discuss BrO, they examined BrOBr and OBrO in detail. A measured enthalpy of formation of OBrO(cr) was noted. Brief mention was made of BrO₃, Br₂O₅, and Br₃O₈, although it was clear that the authors were not convinced that these "compounds" existed.

A 1972 review by Brisdon,¹² discussed seven bromine oxide species: BrO, OBrO, BrOO, BrO₃, BrOBr, Br₂O₂, and Br₂O₄. Whereas there was a complete spectroscopic characterization of BrOBr presented, only a partial identification of BrO was made. General comments proposing the existence (or nonexistence) of the remaining compounds were made.

Clyne and Curran¹³ surveyed the reaction kinetics of halogen atoms, excited molecular halogens, and halogen oxide radicals. The authors covered the literature through early 1976. Their discussion provided a summary of the bimolecular reactions of CIO and BrO with a variety of species. In the case of BrO, one of the products formed was BrOO. Thermodynamic enthalpies of reaction given in this review were extracted from earlier studies by Clyne.

Bromine and its oxides were reviewed (through 1992) by Keller-Rudek *et al.*¹⁴ for the Gmelin series. An earlier review by Kotowski *et al.*¹⁵ for this series was published in 1931. The Keller-Rudek review discussed in detail many oxides [BrO, BrO₂, BrO₃, Br₂O, BrBrO, Br₂O₂, Br₂O₃, Br₂O₄, Br₂O₅, and Br₂O₆], but only briefly mentioned others [BrO₄, BrO₆, Br₂O₇, Br₃O₈, Br₄O, Br₄O₂, and Br₄O₄]. Four species were listed in this review for which we do not have bibliographies. Two of these species [Br₄O, BrO₆] were stated to be weak complexes, whereas the other two [Br₄O₅, Br₄O₄] were assumed to be unstable intermediates. On the other hand, this JPCRD article mentions two species [BrOO, $O_2BrOBrO$] which were not discussed by Keller-Rudek *et al.*¹⁴

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

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

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

Postulated: BrO₃; BrO₄; BrO₆; Br₂O₂

Observed as crystalline solid: OBrOBrO: BrOBrO₂: O₂Br-BrO₂; O₂BrOBrO; BrBrO₄; Br₂O₅

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

In the following discussions, analyses and calculations, the 1993 atomic weights of the elements¹⁶ are used: A_r (Br) = 79.904±0.001; A_r (O)=15.9994±0.0003. Since the mid-1950s, the relative atomic weight of oxygen has changed by 0.0006 to 15.9994. Similarly for bromine, the relative atomic weight has changed by 0.012 to 79.904. Relatively speaking, these changes are sufficiently small that we will not consider any conversions due to relative atomic weights.

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

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

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

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

The NIST–JANAF Thermodynamic Tables (Sec. 6) are calculated using the current atomic weights and fundamental constants, as well as the thermochemical tables for the monatomic and diatomic bromine and oxygen. These latter reference state thermochemical tables, as originally calculated, were based on the 1973 fundamental constants¹⁸ and the 1981 relative atomic weights.¹⁹ This will cause a slight offset in the formation properties of the order 0.01 kJ/mol; such an offset is well outside the uncertainty range of the enthalpy of formation of the bromine oxides. Neumann²⁰ has presented an identical thermochemical table for BrO(g); this table was prepared jointly with this author.²¹

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2. Chemical Species Coverage

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

3. Historical Perspective of the Bromine Oxides

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

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

In the time period 1927 to 1946 (the 3rd and 4th Collective Indices), Chemical Abstracts listed a total of ten citations dealing with bromine oxides. All citations can be grouped in two classes: (1) preparation of solid bromine oxides (from the reaction of bromine and ozone) and (2) preparation of Br_2O in CCl_4 solutions (from the reaction of bromine with HgO). It is not always clear whether the studies' prime motive was the preparation of bromine oxides or the decomposition of O_3 . In all cases, the stability of the products was examined. The first citation (by Lewis and Schuma-

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

^aA secondary formula is intended to suggest the assigned structure. If there is no secondary formula given, this means that no structure has been determined for this species, but the atomic ratio is known.

^bIf no CA Registry Number appears in this column, the species is assumed not to exist.

cher in 1928) dealt with a study in which, upon mixing bromine and ozone in a flask (no temperature specified), a white deposit appeared. Soon thereafter, an explosion destroyed the apparatus. With such an auspicious debut, further studies of the bromine reaction with ozone were performed more carefully and at lower temperatures (15 °C).

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

For the time period 1962 to 1971 (the 7th and 8th Collective Indices), 37 references were cited. The dominant theme was the formation of a particular bromine oxide species through radiolysis, photolysis, or shock waves of solutions of bromates (BrO, BrO₂, BrO₃) and EPR studies of γ -irradiated crystalline bromates (BrO, BrO₂, BrO₃, and BrO₄). There was some additional information on the spectroscopic properties of BrO(g), BrO₃, and Br₂O.

TABLE 2.1. Bromine oxide species.

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

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

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

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

4. Summary of the Data for the Bromine Oxide Species

4.1 Spectroscopic Information

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

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

4.2 Thermodynamic Information

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

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

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

5. Discussion of the Literature Data

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

Early studies, prior to 1960, which deal with the bromine oxides fall into three categories: (1) the reaction of bromine with ozone at low temperatures (< -40 °C), (2) the bromine sensitized decomposition of ozone, and (3) the reaction of bromine with HgO. In the former case, depending on the temperature and relative concentration of the two gases, the products have been stated to be Br₃O₈, BrO₃, Br₂O₅, Br₂O, and BrO₂, all in the condensed phase. However, due to the instability of these oxides and the lack of definitive characterization of the crystals, it was not possible to clearly define the reaction and its products. Reproducibility appeared not to be commonplace. It was also stated that BrO₂ decomposed to Br₂O as the temperature was raised above -40 °C, with Br₂O₇ proposed as an intermediate. Since the

actual chemistry is not of prime importance in this article, and the fact that the characterization of the compounds is not definitive, these articles will not be discussed or critiqued in detail in the sections dealing with these six species.

The early studies revealed the presence of condensed phase products which were stable only at low temperatures, typically below 15 °C. Three articles by Lewis and coworkers examined the reaction of ozone and bromine to form an unstable oxide which they interpreted to be $(Br_3O_8)_n$. Schwarz and co-workers examined reaction schemes which produced BrO₂, Br₂O, and Br₂O₇. Zentl and Rienacher and Brenschede and Schumacher prepared Br₂O by the reaction of bromine vapor on specially prepared HgO and HgO in CCl₄ solution, respectively. As already stated, these reaction schemes produced products which were unstable above approximately 15 °C. In fact, the species of presumed composition Br₃O₈ was found to be very unstable, explosively unstable. This compound was later shown to be most likely BrO_3 . These early preparative reports gave no quantitative information, other than a temperature at which a (presumed) compound appeared to decompose. The reason for emphasizing these points is that, even to the present, most reaction schemes for any of the bromine oxides still rely on the reaction of bromine gas and ozone in the gas phase or solution. Isolation and characterization is difficult and has led to ambiguous results.

5.1 BrO

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

1. Spectroscopy:

Cross sections -[88WAH/RAV], [77VOG/DRE] Microwave -[74LOV/TIE]. [69POW/JOH], [72AMA/YOS], [80LOE/MIL], [81COH/PIC] IR -[78TEV/WAL], [81MCK], [84BUT/KAW], [91ORL/ BUR] UV (emission) -[37VAI], [38VAI], [47COL/GAY] UV (absorption) -[50HER], [58DUR/RAM], [58ZEE], [80LOE/MIL], [81BAR/COH], [85DUI/HUD] Other -[72YAN], [73BYB/SPA], [73PAN/MIT], [74DHA/ CLE], [74DHA/CLE2], [74TIS], [81DOR/MEH], [81GRO/LAU]. [85POY/PIC]. [88IGE/STO]. [89BOW/BOY], [93MON/STI]

2. EPR -

[66CAR/LEV], [67CAR], [67CAR/LEV], [67CAR/ LEV2], [67CAR/LEV3], [67CAR/LEV4], [69CAR], [70CAR/DYE], [71MIL], [71BYF/CAR], [72ADL], [72BRO/BYF], [75DAL/LIN], [86BYB], [86BYB2]

3. Dissociation energy/IP/EA -

[47COL/GAY], [48GAY], [50BRE/BRO], [50HER], [53BRE], [53GAY], [54COT], [58BRE], [58DUR/ RAM], [63SCH], [65GLU/MED], [66VED/GUR], [68GAY], [68WAG/EVA], [69BRE/ROS], [70DAR], [77GLI], [77VOG/DRE], [78DUN/DYK], [79HUB/ HER], [81BOH/SEN], [82WAG/EVA], [84SAU/TAT], [86GIN], [97BAS/GAV], [88IGE/STO], [88SIN], [88TYK], [89GUR/VEY]; [92GIL/POL], [94RUS/ BER]

4. Formation/decomposition/reaction/detection -

[40MUN/SPI], [60BRI/MAT], [60MAT/DOR], [6IGUE/GOU], [62GUE/PAN], [63BUR/NOR], [64TRE/YAH], [66BUX/DAI], [68BUX/DAI], [70TOM/STU], [70AMI/TRE], [71KAU/KOL]. [71OSL], [73DIX/PAR], [73PAR/HER], [74CAH/RIL], [77GIL/GAR], [77TAD/SHI], [78TEV/WAL], [80SEH/ SUD], [80YUN/PIN], [86BRU/AND], [86KRE/FAB], [86RAZ/DOD]. [86HIL/MCC], [89BAR/BEC], [90SOL], [91ARS/ZIV], [91JAD/LON], [91NEU/ DOR], [91SZA/WOJ], [92FAN/JAC], [92MCC/HEN], [92WAT], [94ARP/JOH], [94COX/COX], [94GAR/ SOL], [94HAU/PLA], [94INO], [94MAR/COR], [94POM/PIQ], [95FLE/CHA]

5. Kinetics -

[70CLY/CRU2], [70BRO/BUR]. [70CLY/CRU], [71CLY/CRU], [75CLY/WAT], [75RAD/WHI]. [75WOF/MCE], [76CLY/MON], [76MOI/YUR], [77CLY/CUR], [77CLY/WAT], [79LEU], [79WAT/ SAN], [80JAF/MAI], [80MOL/MOL], [80NIC]. [80SAN], [81CLY/MAC], [81DON/ZEL], [81MEN/ SAT], [81RAY/WAT], [81SAN/RAY], [81SAN/WAT], [82ANT], [82COX/SHE], [82COX/SHE2], [82FER/ SMI], [83BUT/MOR], [82BAU/COX], [84CLA], [85BYK/GOR], [86BRU/STI], [86MCE/SAL]. [86MOX], [86SAN], [86TUN/KO], [87ELO/RYN], [87/HIL/CIC], [88BAR/SOL], [88BRU/TOO], [88HIL], [88HIL/CIC], [88SAL/WOF], [88SAN/FRI], [88TOO/ AND], [88TOO/BRU], [89AND/BRU], [89ATK/BAU], [89ATK/BAU2], [89AUS/JON], [89FRI/SAN], [89KO/ ROD], [89MEL/POU], [89SAN/FRI], [89SOL/SAN], [90DAN/CAR], [90PHI], [90POU/LAN], [90POU/ LAN2], [90TUR], [90TUR/BIR], [91AND/TOO], [91BAR/BAS], [91LAN/LAV], [91MUR], [91TUR], [91TUR/BIR]. [92POU/PIR], [92ROS/TIM]. [92WAH/ SCH], [93BRI/VEY], [93CUR/RAD], [93MAU/WAH], [93WIN/NIC]. [93THO/DAY], [93SAL/WOF], [94CHI/CAR], [94THO], [94TOU], [94WEN/COH], [95THO/CRO]

6. Review -

[48GAY], [50BRE/BRO], [53BRE], [53GAY],

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

Source	⁷⁹ BrO	⁸¹ BrO	Comments
58DUR/RAM	0.455	0.472	<i>B</i> determined by plotting $\nu_{R(J)}$ vs $(J-2)^2$
69POW/JOH	0.4277893 ±0.0000037	0.4260164 ± 0.0000030	$B_{\rm eff}$; microwave spectrum
72AMA/YOS	0.4277789 ±0.0000017	0.4260037 ± 0.0000030	$B_{\rm eff}$; reported in MHz; microwave spectrum
74TIS	0.4282 ± 0.0005	0.4264 ± 0.0005	Review
81COH/PIC	0.42960660 ± 0.00000013	0.42782007 ± 0.00000013	$B_{\rm eff}(B_{\rm e2})$; rotational spectrum
81MCK	0.42960660 ± 0.0000013 0.426278	$0.42782007 \pm 0.00000013$ 0.424510	$B_{\rm eff}$; values taken from 81COH/PIC; held fixed in this spectral analysis; B_0 values
84BUT/KAU	0.42778722 ±0.00000007	0.42601182 ± 0.00000007	$B_{\rm eff}(B_0)$; states this values (from infrared and microwave data) to be same as that derived by 81COH/PIC
91ORL/BUR	0.42778706 ± 0.00000025	0.42601176 ±0.00000011	derived from infrared measurements

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

Spectroscopic Information

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

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

Durie and Ramsay [57RAM, 58DUR/RAM] observed the absorption spectra of BrO during the flash photolysis of Br₂-O₂ mixtures. Twenty absorption bands were recorded in the region 2890–2550 Å. Rotational and vibrational analyses were performed, leading to values for r_0 , and B_0 , as well as ω_e and $\omega_e x_e$ values. Only approximate rotational constants were observed:

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

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

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

Powell and Johnson [69POW/JOH] detected the microwave spectra of the gas phase BrO radical in the ${}^{2}\Pi_{3/2}$ ground state. They reported rotational constants $B_{eff}({}^{79}BrO)$ = 12824.80±0.11 (0.42779 cm⁻¹) and $B_{eff}({}^{81}BrO)$ = 12771.65±0.09 (0.42602 cm⁻¹). These results are in good agreement with the EPR measurements which are mentioned later in this section.

Using microwave detection techniques, Amano *et al.* [72AMA/YOS] determined the equilibrium structure and dipole moment of the gas phase BrO. They reported $B_{\rm eff}$ (⁷⁹BrO, ${}^{2}\Pi_{3/2}$, $\nu=0$)=12824.49±0.05 MHz (0.42779 cm⁻¹) and $B_{\rm eff}({}^{81}$ BrO, ${}^{2}\Pi_{3/2}$, $\nu=0$)=12771.27±0.09 MHz (0.42600 cm⁻¹). The authors recommended $r_{\rm e}$ =1.7171 ±0.0013 Å for both isotopic species as derived from $B_{\rm e}$.

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

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

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

Dhar and Cleveland [74DHA/CLE, 74DHA/CLE2] pre-

sented calculations relating the Morse-potential energy function with force constants, vibrational frequencies and dissociation energies. Calculations refer back to the Durie and Ramsay (1958) study. No new data were provided.

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

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

Tevault *et al.* [78TEV/WAL] studied the reaction of atomic and molecular bromine with atomic and molecular oxygen in argon matrices (photolysis of bromine and ozone containing matrices). Several bromine oxygen compounds were stated to have been formed and identified by infrared spectroscopy—BrO, OBrO, BrBrO, BrOBr, and (BrO)₂. The authors assigned a very weak absorption at 729.9 cm⁻¹ to BrO. The force constant calculated from this frequency was 4.18 mdyn/Å, a value which was not unexpected on the basis of the FO and ClO constants of 5.41 and 4.66 mdyn/Å respectively, obtained from their argon matrix frequencies. A reinterpretation of the data yielded $\omega_e = 751 \text{ cm}^{-1}$ and $\omega_e x_e = 5.0 \text{ cm}^{-1}$ for the ground state. The excited state was reported to lie at 27740 cm⁻¹.

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

The absorption spectra and rotational analysis of the $A^2\Pi_i - X^2\Pi_i$ state of isotopically enriched ⁸¹BrO and normal BrO have been obtained by Barnett *et al.* [81BAR/COH] using the flash photolysis of mixtures of bromine and ozonized oxygen. The authors quoted and used [81MCK]'s value of -968 cm^{-1} as the spin splitting in the ground state. The lower state rotational constants were taken to be those derived from the microwave study [81COH/PIC]. The rotational constants for the excited state were estimated as: $B'_3 = 0.314 \text{ cm}^{-1}$ and $\alpha'_e = 0.0034 \text{ cm}^{-1}$, with an internuclear distance of 1.95 Å. From the analysis of vibrational assignments for BrO, a value for $\Delta G''_{1/2}$ of 722.1±1.1 cm⁻¹ was obtained. Molecular constant values of $\omega''_e = 730.6 \text{ cm}^{-1}$, $\omega'_e = 516.1 \text{ cm}^{-1}$, and $D''_e = 19.694 \text{ cm}^{-1}$ were used for the calculations of the ν' and ν' bands.

Rotational spectrum of the $\nu=0$ and 1 bands and molecu-

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

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

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

Using laser magnetic resonance spectroscopy on three CO₂ laser lines, McKellar [81MCK] detected magnetic dipole transitions between the ²Π_{1/2} and ²Π_{3/2} components of the ground state of BrO. This was the first direct observation of the ²Π_{1/2} state of BrO. A spectrum lying between 964.77 and 969.14 cm⁻¹ was recorded for this state. The spin-orbit splitting parameter A and rotational constants $B^{\rm eff}({}^{2}\Pi_{1/2})$ were determined to be -967.9831 cm⁻¹ (⁷⁹BrO), -967.9981 cm⁻¹ (⁸¹BrO) and 0.4248 cm⁻¹ (⁷⁹BrO), 0.4230 cm⁻¹ (⁸¹BrO), respectively. The author also predicted microwave rotational transition frequencies for the X²Π_{1/2} state of BrO.

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

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

Source	Species	B_0/cm^{-1}	A/cm^{-1}	<i>r</i> ₀ /Å
66CAR/LEV	⁷⁹ BrO	0.45	· · · · ·	
	⁸¹ BrO	0.47		
70CAR/DYE	⁷⁹ BrO	0.4282 ± 0.0005	-815 ± 120	1.720 ^a
	⁸¹ BrO	0.4264 ± 0.0005	-815 ± 120	
71MIL	BrO	adopted values of [700	CAR/DYE]	
72ADL	BrO	adopted values of [700	CAR/DYE]	
72BRO/BYF	⁷⁹ BrO	0.4281	-980	
	⁸¹ BrO	0.4263	-980	
81MCK	⁷⁹ BrO	0.4278 ^b	-967.983(2)	
	⁸¹ BrO	0.4260 ^b	-967.9981(2)	

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

^aUnspecified which BrO isomer (⁷⁹BrO or ⁸¹BrO) it dealt with.

^bThese values are $B_{\rm eff}({}^{2}\Pi_{3/2})$.

value differed from the 722 cm⁻¹ value proposed by [78TEV/WAL, 81BAR/COH, 84BUT/KAW], and the F² Σ (ω_e =822 cm⁻¹), E² Σ (ω_e =897 cm⁻¹), and G²(Δ G_{1/2}=848 cm⁻¹) values for the Rydberg states. Values for E² Σ (ω_e x_e = 2.6 cm⁻¹) were also given.

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

Ground-state properties of the fourth row main group monohydrides XH and monoxides XO (X=K through Br) were determined by Igel-Mann *et al.* [88IGE/STO] by means of self-consistent field/configuration interaction (SCF/CI) calculations. Bond lengths $r_e=1.741$ Å (3.29 a.u.), dissociation energy $D_e=10646$ cm⁻¹ (1.32 eV) and vibrational frequency $\omega_e=726\pm10$ cm⁻¹ were calculated. The authors referred to the dissociation energy recommended by Huber and Herzberg (1979).

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

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

The $\nu = 1-0$ band of BrO in the X²\Pi_{3/2} spin state was measured by Orlando *et al.* [91ORL/BUR] using highresolution Fourier transform absorption spectroscopy. The values obtained were $\nu_0 = 723.414$ (⁷⁹BrO) and $\nu_0 = 721.927$ (⁸¹BrO). One hundred and thirty transitions were assigned and analyzed to determine the band origins and rotational constants of ⁷⁹BrO and ⁸¹BrO. The BrO line positions were fit using the same expression as [84BUT/KAW]. The fits also included the microwave data of [81COH/PIC]. This fit involved the band origin rotational constant and centrifugal distortion constant. UV measurements recorded an A²Π– X²Π transition of BrO in the region 285–355 nm (28169– 35088 cm⁻¹). Rotational constants. $B_0=0.42778706$ (^{79}BrO) and $B_0 = 0.42601176$ (⁸¹BrO) were also obtained. The molecular constants are in good agreement with those reported by [84BUT/KAU].

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

EPR Information

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

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

- 66CAR/LEV A preliminary EPR study in which techniques for measurements were given for BrO. Eighteen lines of the 24 expected were detected, the remaining being obscured by the intense spectrum of O₂. The authors were confident that the spectrum arises from BrO (${}^{2}\Pi_{3/2}$) in its lowest rotational level. The data were consistent with Durie and Ramsay's (1958) calculations for the rotational constant B_0 =0.45 (79 BrO); =0.47 (81 BrO).
- 67CAR A review article of EPR and other forms of microwave spectroscopy in which the BrO spectra was mentioned but no data was given.

- 67CAR/LEV Attempted to study the EPR gas phase spectra of BrO. The relatively weak BrO lines were often obscured by the many intense O_2 lines which occur in the same field region.
- 67CAR/LEV2 The effects of an electric field on the electron resonance spectra in the gas-phase were used to measure the dipole moment of BrO in its electronic ground state.
- 67CAR/LEV3 Examined the EPR spectrum of BrO and detected double quantum transitions.
- 67CAR/LEV4 A gas phase EPR cavity was developed which allows the application of a parallel Stark field. The spectra of BrO were observed clearly in the presence of O₂.
- 69CAR High-resolution spectroscopic studies of the rotational levels of BrO. The author reviewed his previous studies involving the ${}^{2}\Pi_{3/2}$ electronic state of BrO.
- 70CAR/DYE The gas phase EPR spectra of BrO in its ${}^{2}\Pi_{3/2}$, J=3/2 levels were described. The analysis confirmed that the radical has a ${}^{2}\Pi_{3/2}$ ground electronic state (8612.200 MHz). Values of the fine-structure splitting $A = -815\pm120$ cm⁻¹ and rotational constant $B_{0}=0.4282 \pm 0.0005$ cm⁻¹ (79 BrO); =0.4264±0.0005 cm⁻¹ (81 BrO) were obtained. The determination of A as negative showed conclusively that the ground state was ${}^{2}\Pi_{3/2}$ (an inverted doublet). The authors favor their values over those obtained by 58DUR/RAM, leading to a calculation of $r_{0}=1.720$ Å.

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

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

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

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

Although secondary references imply that the article by

[75DAL/LIN] deals with BrO, in fact it examines the EPR of BrO_2 , BrO_4 , and BrO_6 and is strictly a theoretical study.

Byberg [86BYB] studied the EPR of [XO, O₂], X=Br, Cl, formed from the decomposition of ClO₃⁻ and BrO₃⁻ in solid KClO₄:KBrO₃. The main features of the spin Hamiltonian [BrO, O₂] correspond to BrO (²Π) in a crystal field, coupled through an isotropic exchange interaction to O₂ (³Σ_g⁻) to form a spin-doublet ground state. Hamiltonian values were given as experimental and calculated values at 26 K. Molecular hyperfine parameters in MHz for ⁷⁹BrO in the gas phase were also given.

In a subsequent study by Byberg [86BYB2], the preparation of BrO in the crystal state was examined. The EPR and x-irradiation of solid KBrO₃ is shown to produce complex defects of the composition [BrO, O₂]. The EPR spectra of KBrO₃(cr) recorded at 26 K after x-irradiation contained signals from at least six defects in spin-doublet and ground state. But the thermal formation of [BrO, O₂] in the photolyzed KBrO₃(cr) indicated that BrO₃^{*} produced [BrO, O₂] by reaction with a photoinduced precursor R, BrO₃^{*}+R \rightarrow [BrO, O₂]. (See Table 5.1.2.)

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

Dissociation Energy Studies

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

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

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

TABLE 5.1.3. Dissoc	ciation energy of Bro	$D(D_0^{\circ}).$		
Source	eV	kcal/mol	kJ/mol	Comments
Experimental				
47COL/GAY		40.7	170	See discussion
58DUR/RAM		55.3	231	See discussion
Calculation				
77GLI		50.9	213	Used experimental ΔH_f values to calculate mean bond dissociation energies; the calculated D_1 value was derived from a ΔH_f value of [SBRE] but this latter value was not reported.
88IGE/STO	1.32		127	SCF/CI calculations of the fourth row main group oxides (for the oxides K through Br the D_e values are consistently underestimated except for KO); dissociation energy value compared with a 2.45 eV value presumably from [79HUB/HER] (This is not what appears in these authors' book); bond length $r_e=1.741$ Å and vibrational frequency $\omega_e=726\pm10$ cm ⁻¹ were also calculated
Comparisons				
77VOG/DRE				Used value extracted from [68GAY]
78DUN/DYK				Photoelectron spectroscopy study of ionization potential: quotes dissociation value of [58DUR/RAM]
81BOH/SEN				Mentioned dissociation energy but did not give a value
84SAU/TAT				Adopted value recommended by [79HUB/HER]
88TYK				Reported values extracted from existent sources; no new data
92GIL/POL				Photoelectron spectroscopic study; no new values given
Re-assignments				N. Part of the second
SUBRE/BRU	2.2		212	Also refers to 1.75 eV as derived from [47COL/GAN]
SIBRE	2.2		212	No value given but reference made to an earlier study [50BRO/BRE]
53GAY	1.8 ± 0.5	42	176 ± 48	Linear Birge-Spone extrapolation (L.B.X.) (ν , 0-7) 2.2 eV, but
				signs of negative curvature: analogy with CIO and IO favors high value: [47COL/GAY]
54COT	2.2		212	Values extracted from [50HER] and [53GAY] respectively:
	1.8±0.5		176±48	spectroscopic evidence is uncertain; Gaydon's upper limit, which agrees with [50HER] LBSX value, is more in accord with $D_c(CIO)$, but even this seems low
58BRE		51	213	Value reported by Brewer with no explanation as to its origin
63SCH	1.8 ± 0.5		176 ± 48	Value extracted from [53GAY]
65GLU/MED		55.3 ± 0.6	231 ± 3	Values based primarily on the study of [58DUR/RAM]
66VED/GUR		55.3 ± 0.6	231±3	Extrapolation of A ² Π levels; assumed dissociation limit goes to $Br(^{2}_{3/2})+O(^{1}D)$; interpretation taken from Gurvich's early review (1962).
68GAY	2.40 ± 0.02	55.2	231	L.B-S.X ² II 2.7 eV. Good G.BS.A ² II, assuming limit is to $O(D) \ge 40 \pm 0.22$ [SRD118/R AM]
68WAG/EVA		55.3 ± 0.6	231 ± 3	Results based solely on the work of [58DUR/RAM]
70DAR		55.2	231	Spectroscopy, adopted [58DUR/RAM] value:
		55.3 ± 0.6	231 ± 3	Extrapolation of $A^2\Pi$ [66VED/GUR]:
		55.27	231	Extracted from[65WAG/EVA];
		55.3 ± 0.1	231 ± 1	Recommended by [70DAR]
79HUB/HER	2.39 ± 0.01		230.6 ± 1.0	Taken from near convergence of the absorption bands $A - X_1$; assumes dissociation of A into $Br({}^2P_{3/2}) + O({}^3D_2)$
82WAG/EVA		55.3 ± 0.6	231 ± 3	Results based solely on the work of [58DUR/RAM]
89GUR/VEY		55.28 ± 0.6	231.3 ± 3	Based on short extrapolation of the levels in the $A^{-}\Pi_{i}$ state; authors
94RUS/BER		55.3 ± 0.6	231±3	Value given at 0 K; source of value unknown

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

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

5.2. BrO₂ (OBrO)

All references dealing with BrO2 are listed in the following eight categories. This listing is somewhat arbitrary but is intended to give the reader a purview of the reported data. Of prime interest for this article are the spectroscopic and bond dissociation energy studies.

1. Formation/preparation/decomposition

[37SCH/SCH],	[38SCH/WIE],	[39SCH/JAB],
[39SCH/WIE],	[40MUN/SPI],	[59SCH/JOE],
[62GUE/PAN],	[71SHE/TUR],	[74SOL/KEI],
[80JAF/MAI], [83	BUT/MOR], [90LE	EV/OGD]
	and the second	

 Formation in crystal matrix or solution -[62BOY/GRA], [68BUX/DAI], [69AMI/CZA], [69BAR/GIL], [70AMI/TRE], [71OSL], [91SZA/ WOJ]

3. BrO₂ as an intermediate -

[85BEN/KRI], [85STE], [86BEN/KRI, [90SAS/HUI] 4. Reaction -

[53PFL], [55PFL], [72FIE/KOR], [76HER/SCH], [78FOE/SCH], [80FOE/LAM], [80FOE/LAM2], [82FOE/LAM], [82FOE/LAM2], [82FIE/RAG], [83FIE/RAG], [83FOE/LAM], [85FOE/LAM], [86HUI/NET], [88NET/HUI], [89FOE/NOS], [91SZA/WOJ], [94HJE/ROS]

 Enthalpy of formation/bond dissociation energy -[51PFL/SCH], [54COT], [66VED/GUR], [68WAG/ EVA], [82WAG/EVA], [89STA], [95HUI/LAS]

6. Spectroscopy/structure -

[73BYB/SPA], [73PAS/POT], [76PAS/PAV], [78TEV/WAL], [83BUT/MOR], [89BOW/BOY], [94RAT/JON], [95MAI/BOT], [95MUE/MIL] 7. EPR -

[66CHA/BOY], [70COL/COS], [71BYB], [72RAO/ SYM], [75BYB/LIN], [75DAL/LIN], [77SAS/RAO], [79CAR/SAH]

8. Review -

[60GEO], [63SCH/BRA], [72BRI], [84BUR/LAW], [84JAC], [90JAC], [94JAC]

BrO₂ was first mentioned in the literature in 1937 [37SCH/ SCH]. Schwarz *et al.* [37SCH/SCH], [38SCH/WIE], [39SCH/JAB], [39SCH/WIE] discussed the preparation of BrO₂.

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

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

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

The remaining studies of the formation of BrO_2 are based on variations of these above-mentioned procedures. Solomon and Keith [74SOL/KEI] made several attempts to prepare BrO₂, including the glow-discharge method of [37SCH/SCH]. The techniques used produced bromine oxides of variable composition including BrO₂, BrO₃ and BrO_{2.71} (very close to Br₃O₈). Much of this work was reviewed by [63SCH/BRA] and [72BRI], as well as in the Gmelin series mentioned in the Introduction.

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

Chase and Boyd [66CHA/BOY]: radiolysis of crystalline alkaline earth bromates by cobalt-60 γ -ray, suggested that BrO₂ was produced and stabilized in the crystal lattice.

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

Byberg [71BYB]: x-ray irradiated KBrO₄ crystals at 10 or 26 K, spectra interpreted to indicate the existence of BrO_4 which then, thermally dissociated to BrO_2 .

Rao and Symons [72RAO/SYM]: x-ray irradiated crystalline bromates, EPR spectra of BrO₂ in part based on seeing the effects of two isotopes ⁷⁹Br and ⁸¹Br, both having I=3/2, proposed a formation route for BrO₂, results stated to differ from the Collins *et al.* [70COL/COS] data.

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

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

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

Carlier *et al.* [79CAR//SAH]: EPR of BrO₂, spectrum was similar to that observed by [72RAO/SYM].

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

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

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

		Bond	Distan	ce <i>r</i> (Å)	Vibrat	tional	Frequ	encies	
Source	Structure	Br-O	0-0	Br-Br	ν_1		ν ₂	<i>ν</i> ₃	Comments
BrO ₂ (OBrO) 73BYB/SPA	C _{2v} , 117.6°	1.625							Modified extended Huckel theory used to calculate nuclear quadrupole coupling constants; calculated values for structure
73PAS/POT									Raman spectra in crystalline form indicated that BrO_2 exists as Br_2O_4 with a Br–Br bond
78TEV/WAL	*110±2°							852	Infrared spectra of the isolated radical in an Ar matrix; *apex angle determined on identification of ν_3 asymmetric stretch; ¹⁸ O isotopic enrichment experiments used to identify molecules
83BUT/MOR	C _{2v} , 118°	2.9							Mass spectrometry; discharge-flow system; reaction of $O+Br_2$; assumed structure (in analogy with OCIO) and calculated rotational constants
84JAC, 90JAC 94JAC								852	Review recommended ν_3 value from Ar matrix study of 78TEV/ WAL
89BOW/BOY	C _{2v} , 117.6°	1.625							SCF multiple scattering X- α calculations of the bonding and nuclear quadrupole coupling in BrO ₂ ; adopted geometry of [73BYB/SPA]
95MAI/BOT	<i>C</i> ₂ <i>v</i>				O ⁸¹ Br 791–7 O ⁷⁹ Br 794–7	·O 97 ·O 99		O ⁸¹ BrO 842–844 O ⁷⁹ BrO 845–847	IR absorption; matrix isolation at 12 K
95MUE/MIL	C _{2v} , 114.4°	1.649							Microwave study, preliminary analysis also supportive of ν_2 approximately equal to 300 cm ⁻¹
BrOO 70CLY/CRU									Electronic absorption spectrophotometry in a discharge-flow system of BrO; formation of BrOO in BrO+BrO- $k_2 \rightarrow Br+BrOO \rightarrow Br+O_2$ disproportionation reaction
78TEV/SMA					1487	,			Infrared spectra of the isolated radical in an argon matrix
79MIC/PAY					872		100		BEBO calculations, stated to be indeterminate for the bending frequency; value suggested for ν_2 is consistent with the authors' kinetic data in the region 200–360 K
83BUT/MOR	C _s , 120°	2	1.5						Mass spectrometry, discharge-flow system; assumed structure (in analogy with $Br-O-O-Br$ structure suggested by 70CLY/CRU) and calculated rotational constants
84JAC, 90JAC					1487	7			Review recommended $\nu_{\rm I}$ value from Ar matrix study of 78TEV/ SMA
95MAI/BOT	Cs				Br ¹⁶ C 1475.5–1 Br ¹⁶ O ¹ 1430–14) ₂ 484.0 ⁸ O 132.1			IR absorption; matrix isolation at 12 K; the vibrational frequency assigned to $Br^{16}O^{18}O$ is in fact a mixture of $Br^{16}O^{18}O$ and $Br^{18}O^{16}O$
BrO ₃					ν,	ν2	ν	$_{3} \nu_{4}$	
56VEN/SUN	C ₃₀ , 89°	1.68		<u></u>	442	800	3:	5 828	References observed Raman frequencies, however it appears adopted frequencies are approximations derived from the ion; bond distance calculated by Badger's rule; calculation of force constants
63VEN/RAJ	C _{3v} , 89°				442 439	800 806	3: 0 3: 0	5 828) 815 5)	Urey-Bradley potential force field; although the authors refer to observed vibrational frequencies there is no specific reference to these observations; observed and calculated frequencies given respectively; calculation of force constants
64RAO/SYM	C_{3v}								Vibrational mean square amplitude theory; two totally symmetric A_1 and identifies six vibrations, modes; no data provided; two doubly

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

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degenerate E mean square amplitudes calculated

Table 6. (Cont	inued.)
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Source	Structure	Br-O	0-0	Br-Br	ν_1	ν2	<i>v</i> ₃	ν_4	Comments
70BEG/SUB	C _{3v} , 114°								ESR; formation of BrO ₃ from γ -radiolysis of potassium bromate at 77 K; structure identified; magnetic parameters given
72RAO	C_{3v}								Centrifugal distortion constants; classifies the six vibrations as two totally symmetric A_1 and two doubly degenerate E modes but no values were given
74BYB/KIR	* <i>c</i> s								*ESR crystal study of paramagnetic defects in x-irradiated KBrO ₃ suggests that the species is BrO_3^- rather than BrO_3 ; KNO ₃ ; KBrO ₃ exhibits the BrO ₃ species with a cylindrical spin Hamiltonian analogous to that of ClO ₃ ; calculated bond distance based on ClO ₃
77LEE/BEN		1.66							EXAFS spectra; prediction of bond length
78THI/MOH	C _{3v} , 89°	1.79			800	442	82 8	350	Group theoretical method; vibrational frequencies calculated for ν_1 and ν_2 are reversed, the same is true for ν_3 and ν_4 ; force constants are calculated
85BYB	C _{3v} , 112°	1.57							Values proposed earlier by 74BYB/KIR to account for the spin Hamiltonian of BrO_3 in KNO_3 : $KBrO_3$;
	105.5°	1.56	1.72	1.64					ESR spectra in $KClO_4$: $KBrO_3$; author proposes a new asymmetric structure for BrO_3 with bond distances for $(Br-O_3')$, $(Br-O_2)$ and $(Br-O_3)$, respectively
86UMA/RAM	C_{3v}								ESR γ -irradiation of crystal KBrO ₃ and Sr(BrO ₃) ₂ ·H ₂ O; MO calculations using the CNDO/2 method; NQR experimental values
BrOBr					ν	1	ν_2	ν ₃	· · · · · · · · · · · · · · · · · · ·
54ANT/DOJ									UV absorption spectra of Br_2O in CCl_4 ; strong absorption band at 2800 Å (35714 cm ⁻¹)
68CAM/JON	C _{2v} , 113°				50)4	197	587	IR spectra of the crystal Br_2O and ${}^{18}O$ -enriched Br_2O ;spectra most satisfactorily explained in terms of C_{2v} symmetry; comparisons with F_2O and Cl_2O were used in explaining data; force constants were calculated
72BRI	113°				50)4	197	583	Review based crystal study by 68CAM/JON; calculation of force constants
77PAS/PAV					50)4	197	590	Raman analysis (species observed in a matrix at 50 °C) corroborates previous IR studies; assumed the formation of Br_2O from decomposition of Br_3O_3
78PAS					50)6		592	IR spectra of the crystal Br ₂ O
78TEV/WAL	87°				52	6.1		504	IR spectra of the isolated radical in an argon matrix: states that the values assigned by 68CAM/JON for ν_1 and ν_3 are reversed and questioned the ν_3 reasonableness of the bond angle: ¹⁸ O isotopic enrichment experiments used
84BOL/BAL	Linear				2:	50	245	800	Extended x-ray absorption spectra of thermally excited vibrations: frequencies were used to calculate force constants; no preferred structure was recommended; estimates of the vibrational frequencies as a function of bond angles
84EPI/LAR									MOVB theory: no data provided
84JAC. 90JAC.					52	6.1		623.4	Review recommended ν_1 and ν_3 values from Ar matrix studies by 78TEV/WAL and 87ALL/POL
94JAC 87ALL/POL	*113° or 87	7°			52	6.1		623.4	IR spectra of matrix isolated radical: *bond angle depend on relative assignment of ν_1 and ν_3
90LEV/OGD	C_{2v} , 112±	2° 1	.85	3.0	7 5	08		595	IR and UV-VIS spectroscopy and bromine k-edge EXAFS of the solid radical: consistent with the results of 68CAM/JON and 78PAS

Table 6. (Continued.)

		Bond I	Distance	r(Å)	Vi	brational	Frequencies	
Source	Structure	Br–O	0-0	Br-Br	ν_1	ν_2	ν ₃	Comments
92NOV	C _{2v} , 115.69°	1.80902						Ab initio calculations and an extended basis set; comparable with the results of 90LEV/OGD
95LEE	C _{2v} , 112.9°	1.865			512	180	613	Ab initio calculations—CCSD(T)
95MUE/COH	C _{2v} , 112.24°	1.8429			•••	180		Microwave spectra for three isotopomers
BrBrO								
73DIX/PAR	150°.							Reaction complex O-Br-Br; plausible triplet ground state at α =180°, however, an improved approximation might change α to 150°
73PAR/HER								Cross-beam experiments involving collision of O atoms with Br molecules; predicts an O-Br-Br nonlinear complex with a triplet ground state
78TEV/WAL					804	<200	236	Infrared spectra of the Ar–Br ₂ –O ₃ matrix isolated radical: the Br–Br bending mode are based on comparison with the Cl–Cl stretch and ClClO bending mode of ClClO
80VEL/DUR								Cross-beam scattering; stated reactive results are consistent with the long-lived triplet of the OBrBr complex as suggested by 78TEV/ WAL and 73PAR/HER
82FER/SMI	³ A"							Reactive scattering of O atoms with Br_2 ; proposed existence of a shortlived OBrBr collision complex with a bent configuration and with a modest E_0 of approximately 110 kJ/mol; supports the conclusion of 73PAR/HER
84JAC, 90JAC, 94JAC 87LOE/AND					804		236	Review recommended ν_1 and ν_3 from Ar matrix study by 78TEV/ WAL Frontier orbital theory and Lewis electronic structure theory; proposed existence of a long-lived intermediate of a cyclic BrBrO structure
95LEE	113°	1.690	2.510		793	215	153	Ab initio calculations—CCSD(T)
Br ₂ O ₂		Br–O	0-0	Br–O				
68EDW/GRE								Rate law stoichiometry; classified as BrBrO2
70CLY/CRU	120°	1.64	1.5	2.0				Electronic absorption spectrophotometry in a discharge-flow system of BrO; transition-state theory; a symmetrical planar bent chain triplet species with a structure (BrOOBr) was assumed; estimated in comparison with ClOOCl
78TEV/WAL								IR argon matrix spectroscopy; photolysis; weak bands appeared at 831.7, 830.2, and 760.3 cm ⁻¹ ; identified the most likely structure of Br_2O_2 as an open chain when the Br–Br bond remains intact (OBr–BrO), and a (BrOBrO) structure formed by the insertion of an oxygen atom into the weakened Br–Br bond
84EPI/LAR								MOVB theory; reference to this species in table but no data provided
Br ₂ O ₃								Descend from the three bolic and the C. D. C. D. C.
/+rA3/rAv								absorption and IR spectra; the vibrational spectrum of Br_2O_1 : Raman absorption and IR spectra; the vibrational spectrum of Br_2O_3 shows the presence of a BrOBr bond but it was not possible to distinguish between the two forms (OBrOBrO and BrOBrO ₂)
76PAS/PAV	Cs							Raman spectra: suggested a (OBrOBrO) structure for Br_2O_3 : some vibrational frequencies have been assigned to specific vibrational modes
77PAS/PAV								Raman spectra; suggested a symmetric structure (OBrOBrO); some frequencies have been assigned to specific vibrational modes
87ALL/POL							973.1-1029.6	IR spectra of a crystalline Br ₂ O ₃ in argon matrix: not able to determine which structure (BrOBrO ₂ or OBrOBrO) existed; the symmetrical structure was adopted based on comparison of Raman spectra of Br ₂ O ₃ and Br ₂ O ₄

Table 6.	(Continued.)
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		Bond	Distance	e r(Å)	Vibratio	nal Fre	quencies	
Source	Structure	Br–O	0-0	Br–O	ν_1	<i>v</i> ₂	ν ₃	Comments
93STI								Proposed anionic structure of Br ⁺ BrO ₃ ⁻ for Br ₂ O ₃
Br₂O₄ 73PAS/POT	C_{2v} or C_2				861-882	205	910-919	Raman spectra at -180 °C;
(O ₂ BrBrO ₂)								Br_2O_4 is classified as having a dimeric structure $(O_2Br{-}BrO_2)$ with a $Br{-}Br$ bond
74PAS/PAV (O ₂ BrBrO ₂) 76PAS/PAV (O ₂ BrOBrO)								Raman spectra; suggested structure to be (O_2BrBrO_2) Raman spectra; suggested structure of the two isomers of Br_2O_4 to be (O_2BrBrO_2) and $(O_2BrOBrO)$; some vibrational frequencies have been assigned to specific vibrational modes of the two symmetric and asymmetric isomers
77PAS/PAV (O ₂ BrOBrO)	C_{2v} or C_2							Raman spectra; suggested structures (O_2BrBrO_2) and $(O_2BrOBrO)$ for the two isomers of $B_{12}O_4$, some frequencies have been assigned to specific modes of the symmetric and asymmetric isomers
92GIL/LEV (BrBrO ₄)	110±3°							Spectroscopic and EXAFS data on solid compound; interatomic distance given
Br ₂ O ₅ 77PAS/PAV								Based on the Raman spectra and structure of Br_2O_3 and Br_2O_4 , an I_2O_5 analogous polymer structure is proposed for Br_2O_5

served the Raman spectra of the crystalline bromine dioxide at -180 °C in a sealed tube *in vacuo*. There is no structural or vibrational information provided directly for BrO₂(g), although tentative assignments had been made for the crystalline dimer.

Tevault *et al.* [78TEV/WAL] studied the reaction of atomic and molecular bromine with atomic and molecular oxygen in argon matrices (photolysis of bromine and ozone containing matrices). Several bromine oxygen compounds were stated to have been formed and identified by infrared spectroscopy — BrO, OBrO, BrBrO, BrOBr, and (BrO)₂. The apex angle of BrO₂ was calculated to be $110\pm2^{\circ}$ based on three facts:

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

Bowmaker and Boyd [89BOW/BOY] assumed the BrO₂ geometry as suggested by [73BYB/SPA] in performing an SCF-X α study of the bonding and nuclear quadrupole coupling in BrO₂. Butkovskaya *et al.* [83BUT/MOR], in their kinetic studies, proposed a C_{2v} structure with a bond angle of 118° and a bond distance of 2.9 Å by analogy with OCIO. This series was detected by modulated beam mass spectrometry. Magnetic and electric field beam focusing revealed that OBrO is a paramagnetic molecule with a C_{2v} symmetry.

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

Rattigan *et al.* [94RAT/JON] observed a visible absorption spectrum arising from OBrO in the bromine sensitized decomposition of ozone. The authors provided spectral evi-

dence for the $A^2A_2 \leftarrow X^2B_1$ electronic transition. They reported $\nu_{0,0,0} = 16178 \text{ cm}^{-1}$ and approximate vibrational frequencies for the excited state ($\nu_1 = 600 \text{ cm}^{-1}$ and $\nu_2 = 200 \text{ cm}^{-1}$).

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

Maier and Bothur [95MAI/BOT] studied the flash photolysis of a gas mixture containing bromine, oxygen and argon. BrO₂ was formed by the matrix irradiation of BrOO. The IR absorption of two isomers (O⁸¹BrO and O⁷⁹BrO) was observed at three different concentration ratios of Br₂/ O₂/Ar and values for ν_1 and ν_3 were assigned.

Pflugmacher *et al.* [51PFL/SCH] experimentally measured the enthalpy of formation of BrO₂ (cr). The value reported was -12.5 ± 0.7 kcal which, in fact, refers to the decomposition heat. The formation reaction is the reverse of what was measured. Wagman *et al.* [68WAG/EVA], [82WAG/EVA], in their reviews, assumed that the measured value referred to the energy of the reaction (not the enthalpy) and corrected the value for a Δ (pv) term, adjusted the value from -45 °C to 25 °C, thus resulting in a value of 11.6 kcal/mol for the enthalpy of formation of BrO₂(cr). Glushko and Medvedev (1965) adopted 12.5 kcal/mol as the enthalpy of formation.

Cottrell [54COT] reported $D(O-BrO) \ge 70 \pm 10$ kcal/mol. (This converts to $\Delta_t H=87.3$ kJ/mol.) This value was based on the enthalpy of formation of BrO₂(cr) reported by [51PFL/SCH] and $D_0(BrO)=2.25$ eV or 50 kcal/mol. Cottrell expressed doubt as to the validity of this value based on comparison with ClO₂. The enthalpy of dissociation reported by [66VED/GUR] is $\Delta H(298) \ge 70$ kcal/mol for the reaction BrO₂ \rightarrow BrO+O. This is an estimated value based on the work by Cottrell (1954). In contrast Huie [95HUI/LAS] has estimated the ethalpy of formation of OBrO(g) in the following manner. According to Stanbury [89STAN], the enthalpy of formation of OBrO in the gas phase can be estimated from the value of $\Delta G^0 = 144$ kJ mol⁻¹ in the aqueous phase by comparison with the gas and aqueous phase values for OCIO. Taking $\Delta G^0 = 120.5$ kJ mol⁻¹ for OCIO(g) and $\Delta G^0 = 117.6$ kJ mol⁻¹ for OCIO(aq) [Wagman, 1968] and assuming the same ratio applies for OBrO, we obtain $\Delta G^0 = 148.0$ kJ mol⁻¹ for OBrO(g) and $\Delta_r H^0 = 130$ kJ mol⁻¹.

5.3. BrO₂ (BrOO)

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

- 1. Formation as an intermediate in kinetic schemes -
- [69IP/BUR], [70BLA/BRO], [70CLY/CRU], [77CLY/CUR], [80JAF/MAI], [81SAN/WAT], [83BUT/MOR], [86SAN], [88TOO/BRU], [93MAU/ WAH]
- Reviews -[77CLY/CUR], [84BUR/LAW], [84JAC], [90JAC], [94JAC]
- Spectroscopy/structure -[70CLY/CRU], [78TEV/SMA], [79MIC/PAY], [83BUT/MOR], [95MAI/BOT]
- 4. Enthalpy of formation/ dissociation energy -
 - [691P/BUR], [70BLA/BRO], [70CLY/CRU], [81SAN/WAT], [83BUT/MOR], [88TOO/BRU], [95HUI/LAS]

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

Michael and Payne [79MIC/PAY] discussed a calculational approach (BEBO) in which they determined ν_1 =872 cm⁻¹. Although this method was stated to be indeterminate for the bending frequency, the authors did suggest that a value of ν_2 =100 cm⁻¹ was consistent with their kinetic data in the region of 200–360 K.

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

Maier and Bothur [95MAI/BOT] studied the flash photolysis of a gas mixture containing bromine, oxygen and argon. BrOO was produced by this process. The IR absorption of three isomers (Br¹⁶O¹⁸O, Br¹⁸O¹⁶O, and Br¹⁶O₂) was observed and values for ν_1 were assigned.

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

Ip and Burns [69IP/BUR] determined the recombination rate constants of bromine atoms in the presence of six different third bodies (helium, neon, argon, krypton, oxygen and nitrogen) over the temperature range of 300 and 1273 K. The authors refer to two earlier studies: Rabinowitch and Wood [36RAB/WOO] and Strong *et al.* [57STR/CHI]. Based on these data, Blake *et al.* [70BLA/BRO] calculated interaction potentials between atomic bromine, oxygen and an inert third body (such as a rare gas). A value was given for Br–O₂. BrOO was thought to be unstable with a bond energy (Br–OO) of approximately 1 kcal/mol which translated to an enthalpy of formation of 108 kJ/mol.

5.4. BrO₃

The articles pertaining to BrO_3 may be classified as follows.

1. Formation/preparation -

- [28LEW/SCH], [29LEW/SCH], [29LEW/SCH2], [30LEW/SCH], [38CSH/WIE], [39SCH/WIE], [40MUN/SPI], [53PFL], [55PFL], [55PFL/RAB], [58ARV/AYM], [59ARV/AYM], [59PFL], [59SCH], [60BRI/MAT], [62GUE/PAN], [74SOL/KEI], [82MUK/KHI]
- Radiolysis -[60MAT/DOR], [62BOY/GRA], [70AMI/TRE], [70BEG/SUB], [71SER/ZAK]
- 3. Spectroscopy/structure -

[56VEN/SUN], [63VEN/RAJ], [64RAO/SAN], [72RAO], [77LEE/BEN], [78THI/MOH], [84SAS/ RAO], [85BYB], [86UMA/RAM] 4. EPR -

- [70BEG/SUB], [71SER/ZAK], [72RAO/SYM], [74BYB/KIR], [85BYB]
- 5. Review -
 - [34BRA], [60GEO], [63SCH/BRA], [80KOL], [84JAC]

6. Enthalpy of formation - [48FAR/KLE]

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

There is no confirmatory information as to the proper characterization. There are many articles dealing with the formation or reaction of BrO₃. Pflugmacher *et al.* [55PFL/RAB] studied the reaction of bromine with excess O₂ in a glow discharge at 0 °C. BrO₃ was claimed to be the product. Although the ratio was 1:3, it is not clear that the product was BrO₃. The compound formed was claimed to decompose above -70 °C. Also, the method of Lewis and Schumacher [29LEW/SCH], in which the reaction of bromine

with ozone was claimed to produce Br_3O_8 , was reproduced here with a larger excess of ozone and yielded BrO_3 (in the condensed phase).

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

Solomon and Keith [74SOL/KEI] made several attempts to prepare BrO_2 , including the glow-discharge method of [37SCH/SCH]. The techniques used produced bromine oxides of variable composition including BrO_2 , BrO_3 , and BrO_{271} (very close to Br_3O_8).

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

BrO₃ was produced by the γ -radiolysis of KBrO₃ at 77 K [70BEG/SUB]. From the EPR measurements of BrO₃ and an assumed C_{3v} symmetry, they calculated the bond angle to be 114°. The structure was distorted in the crystalline environment. The authors stated that the radical must be distorted from C_{3v} symmetry presumably because of an asymmetric environment of the potassium ions around the oxygen atoms of BrO₃. Similar results were reported in 1985 by Byberg [85BYB], in which the author reported that the BrO₃ radical had C_{3v} symmetry but some distortion might occur due to the nature of the host crystal. He discussed a bond angle of 112° and a bond length of 1.57 Å. The other studies provide no additional information.

The spectroscopic articles for the gas phase radical involved force field calculations of pyramidal XY₃ type molecules [56VEN/SUN, 63VEN/RAJ, 64RAO/SAN, 72RAO, 78THI/MOH]. Contrary to the implications of these five articles, there was no observed structural information nor was there any observed vibrational information. Upon examination of the earlier literature cited by these authors, vibrational frequency information was found for BrO_3^- in a crystalline environment. Two of the four vibrational frequencies matched exactly with those reported for BrO_3^- . These articles have assumed a pyramidal structure with an O-Br-O angle of 89° (the same angle was used for the chlorine, bromine, and iodine trioxides): a bond distance Br-O of 1.68 Å (from Badger's rule), and vibrational frequencies (in cm^{-1}) of $\nu_1 = 442$ [A₁], $\nu_2 = 800$ [A₂], $\nu_3 = 350$ [E], and $\nu_4 = 828$ [E].

Two additional studies provide insight into the structure of BrO₃. Electric field gradients at the halogen site in XO₃ and XO₃²⁻ radicals (X=Cl, Br), formed by the γ -irradiation of single crystals of NaClO₃, KClO₃, KBrO₃ and Sr(BrO₃)₂·H₂O have been evaluated by MO calculations using the CNDO/2 method. The symmetry of the XO₃ radicals was assumed to be that of XO₃⁻ ions which have C_{3v} symmetry [86UMA/RAM]. Lee and Beni [77LEE/BEN], in their

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calculation of atomic phase shifts (as applied to extended x-ray absorption and fine structure in molecules and crystals) predicted a Br–O bond length of 1.66 Å in solution. No other information of BrO₃ was provided.

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

5.5. BrO₄

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

BrO₄ has been proposed to be formed:

- (1) As a weak adduct, $BrO \cdot O_3$, in the disproportionation of BrO [90TUR/BIR]
- (2) In the ⁶⁰Co γ -irradiation of an acidic aqueous glass containing perbromate ions [75GIN/SYM]
- (3) In the X-irradiation of KBrO₄ crystals [71BYB]
- (4) As a complex (BrO₂·O₂) during the X-irradiation of KBrO₄ (calculational model and EPR study) [75DAL/ LIN]
- (5) By the X-irradiation of KClO₄ single crystals doped with KBrO₄ [85BJE/BYB]
- (6) During the X-irradiation of KBrO₄ single crystals in which a weakly bound complex $(BrO_2 \cdot 2O_2)$ was formed which decayed to BrO₄ [75BYB/LIN].

5.6. Br₂O (BrOBr)

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

- 1. Preparation/decomposition -
 - [30ZIN/RIE], [31LEW/FEI], [35BRE/SCH]. [36BRE/SCH], [38SCH/WIE], [39SCH/WIE], [40MUN/SPI], [61GUE/GOU], [62GUE/PAN]
- 2. Review -
 - [34BRA], [60GEO], [63SCH/BRA], [72BRI]. [84BUR/LAW], [84JAC], [90JAC], [94JAC]
- 3. Reaction -

[47KLA/BOL], [53KAN], [69JEN/ZIE], [72BUN], [72BUB2], [76ODY/NEC], [79MIT], [89FLE/SWA], [87SWA/FLE], [94DNE/ELI], [95HEU/HAN]

- 4. Spectroscopy/structure -
 - (In solution) -[54ANB/DOS] (In crystal) - [68CAM/JON], [77PAS/PAV], [90LEV/OGD]
 - (In matrix) [78TEV/WAL], [87ALL/POL], [90LEV/OGD]

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

6. Enthalpy of formation -

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

[66CAR/LEV]

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

In a review article, Brady [34BRA] stated that Zintl and Rienacker [30ZIN/RIE] obtained small quantities of a volatile oxide, perhaps Br₂O, by two methods; (1) by passing bromine vapor over a specially prepared HgO at 50-60 °C, and (2) by mixing bromine vapor with ozone under reduced pressure at 0 °C. A subsequent study by Brenschede and Schumacher [35BRE/SCH] examined the reaction between HgO and bromine in a carbon tetrachloride solution. The method of preparation is given, as well as the self decomposition and the reaction with carbon tetrachloride in light [the same reaction occurred in dark in a few days]. The decomposition in light was presumed to be $Br_2O \rightarrow Br_2 + 1/2O_2$ and $Br_2O+CCl_4 \rightarrow COCl_2+Br_2+Cl_2$. A subsequent study by the same authors [36BRE/SCH] examined the same formation reaction. In addition, they studied the extinction curve of Br₂O dissolved in CCl₄ and the thermal and photochemical decomposition.

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

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

Anthar and Dostrovsky [54ANT/DOS] measured the ultraviolet absorption spectra of Br₂O in CCl₄. A strong absorption band was observed at 2800 Å (35714 cm⁻¹).

Parrish and Herschbach [73PAR/HER] observed, in their cross beam experiments, that the reaction of $O({}^{3}P)$ with $Br_{2}({}^{4}\Sigma_{g}^{-})$ yielded $BrO({}^{2}\Pi) \div Br({}^{2}P)$. The authors stated that this reaction occurred "via a persistent collision complex

with large reaction yield and no activation energy, but the known, stable Br_2O molecule does not correlate with the reactants."

The IR spectra of the solid was most satisfactorily explained [68CAM/JON] in terms of a bent triatomic molecule with C_{2v} symmetry and a ν_1 =504 cm⁻¹, ν_2 =197 cm⁻¹, and ν_3 =587 cm⁻¹. The assumed bond angle was 113°.

Pascal *et al.* [77PAS/PAV] assumed that Br_2O was formed from the decomposition of Br_2O_3 . The authors observed the symmetric stretch of Br_2O to be 504 cm⁻¹, the asymmetric stretch, 590 cm⁻¹, and assumed the bend to be 197 cm⁻¹. The Raman analysis of Br_2O corroborated the previous infrared work by Campbell *et al.* In a later study, Pascal [78PAS] reported ν_1 =506 cm⁻¹ and ν_3 =592 cm⁻¹ values.

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

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

Epiotis *et al.* [84EPI/LAR], using a MOVB theory, referred to Br₂O in a table but provided no information.

Allen *et al.* [87ALL/POL] studied the IR spectra of matrix isolated Br₂O and assigned ν_3 to be 623.4 cm⁻¹ and ν_1 to be 526.1 cm⁻¹. The authors referred to a bond angle of 113° or 87° based on the ν_3 isotopic shift information.

Levason *et al.* [90LEV/OGD] studied Br₂O (cr) by infrared and UV-VIS spectroscopy and bromine K-edge extended x-ray absorption fine structure (EXFAS). This is the first definitive structural analysis study for the bromine oxides (Br₂O₃ was definitively analyzed at a later date by others). The authors' results are consistent with the IR spectra of Br₂O obtained by Campbell *et al.* [68CAM/JON]. the ¹⁸O results which demonstrated that solid Br₂O is molecular, and with experiments by Pascal [78PAS] who reported v_1 =506 cm⁻¹ and v_3 =592 cm⁻¹. The data were consistent with C_{2c} symmetry and a bond angle (Br–O–Br) of 112±2° and bond distance r(Br–O)=1.85 Å.

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

Jacox [84JAC], [90JAC], [94JAC], in her reviews, recom-

mended an a_1 symmetric stretch of 526.1 cm⁻¹ (Ar) based on the studies by [78TEV/WAL, 87ALL/POL], and a ν_3 asymmetric stretch of 623.4 cm⁻¹ (Ar) based on the work by [90LEV/OGD]. Jacox did not report a value for ν_2 .

Lee [95LEE], using *ab initio* techniques, calculated the equilibrium structure and harmonic vibrational frequencies of Br₂O. The results suggested a C_{2v} symmetry with a bond angle of 112.9° and a bond distance of 1.865 Å.

Mueller and Cohen [95MUE/COH], from the microwave spectra of three isotopomers of BrOBr(g), determined $r_0=1.8429$ Å and a bond angle of 112.24°. Their study implied $\nu_2=180\pm5$ cm⁻¹.

Novak [92NOV] estimated the enthalpy of formation, $\Delta_f H^{\circ}(Br_2O, 0 \text{ K})=83\pm8 \text{ kJ/mol}$ from a sum of bond enthalpies that were deduced from the data of H₂O and HOBr. The enthalpy of formation corresponds to $\Delta_{at}H^{\circ}(0 \text{ K})=399.6 \text{ kJ/}$ mol or an average bond dissociation energy of roughly 200 kJ/mol. The author did not specify the temperature; we assume T/K-0.

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

Thorn *et al.* [95THO/MON] quoted the enthalpy of formation value derived by [95ORL/BUR] to encompass the range of 113–159 kJ/mol. From a study of the photoionization efficiency spectrum of Br₂O, along with the ionization energy and the appearance energy of BrO⁺, the authors derived $\Delta_{\rm f}H({\rm Br}_{2}{\rm O}, 298 \text{ K})$ =107.1 kJ/mol and $\Delta_{\rm f}H({\rm Br}_{2}{\rm O}, 0 \text{ K})$ =124.1 kJ/mol. The uncertainty was estimated to be ±3.5 kJ/mol.

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

5.7. Br₂O (BrBrO)

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

There are numerous articles which provide specific spectroscopic information:

- Reaction complex OBrBr follows the O+Br₂ reaction -[73DIX/PAR], [73PAR/HER]
- (2) Infrared spectra in an argon matrix [78TEV/WAL]
- (3) Structure in an argon matrix [80VEL/DUR], [82FER/ SMI], [87LOE/AND]
- (4) Reactive scattering of oxygen atoms with chlorine molecules; observed results which are consistent with

OCICI with a ${}^{3}\Pi$ symmetry when colinear and ${}^{3}A''$ symmetry when bent. Browett *et al.* [81BRO/HOB] referred to the analogous O-X-X study as described by [78TEV/WAL] and [73PAR/HER]

- (5) The vibrational frequency information (ν₁, ν₃) was reviewed by Jacox [84JAC], [90JAC], [94JAC] and was based on the data reported by [78TEV/WAL]
- (6) [93SCH/ABD] used Fourier transform infrared (FTIR) techniques to study BrBrO in an argon matrix; their observations supported the conclusions of Tevault *et al.* [78TEV/WAL]
- (7) Burdett *et al.* [84BUR/LAW], in a review, discussed the stability and spectroscopic properties of BrBrO but referred back to the work of [78TEV/WAL] as the only source of information
- (8) Lee [95LEE], using *ab initio* techniques, calculated the equilibrium structure and harmonic vibrational frequencies of BrBrO.

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

Tevault *et al.* [78TEV/WAL] studied the reaction of atomic and molecular bromine with atomic and molecular oxygen in argon matrices (photolysis of bromine and ozone containing matrices). Several bromine oxygen compounds were stated to have been formed and identified by infrared spectroscopy—BrO, OBrO, BrBrO, BrOBr, and (BrO)₂. The authors observed the spectra of BrBrO in a photolyzed Ar-Br₂-O₃ matrix. The assignments were assumed to be ν_1 =804 cm⁻¹ (Br-O stretch), ν_3 =236 cm⁻¹ (Br-Br stretch) and the ν_2 value (the bending mode) was expected to be below 200 cm⁻¹.

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

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

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

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

5.8. Br₂ [O₂]

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

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

The pertinent articles may be grouped as follows:

- 1. Proposed intermediate in aqueous solution -
 - [30BRA], [34SKR], [52EDW], [58SIG], [68BUK/ DAI], [68EDW/GRE], [72FIE/KOR], [73SOK/ DOR], [76HER/SCH], [78ROV/ZHA], [79NOS/ BOD], [86THO]

2. Proposed as intermediate in gas phase reaction systems -

[70BRO/BUR], [70CLY/CRU], [80JAF/MAI], [81SAN/WAT], [83BUT/MOR], [86SAN], [90TUR/ BIR], [93MAU/WAH]

3. Proposed structure -

[30BRA]: BrOOBr or OBrBrO (possible) [52EDW]: Donor-acceptor intermediate BrBrO₂ [66SPR/PIM]: Calculation, BrOOBr (staggered or trapezoidal) [68EDW/GRE]: BrBrO₂ [70CLY/CRU]: Symmetric planar bent BrOOBr (120°) [73SOK/DOR]: BrOOBr [78TEV/WAL]: Possibly OBr-BrO or BrOBrO [80JAF/MAI]: Possibly staggered or trapezoidal (Br-O-O-Br) [81SAN/WAT]: Trapezoidal (Br-O-O-Br) [86THO]: BrOOBr [90TUR/BIR]: BrOOBr [93MAU/WAH]: BrOOBr 4. Spectroscopy -

[78TEV/WAL], [93MAU/WAH]

5.9. Br₂O₃ (OBrOBrO)

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

1. Dissertations (full copy not available at this time) - [66CAM], [78PAS], [83ALL]

2. Formation with crystal characterization -

[74PAS/PAV], [76PAS/PAV], [77PAS/PAV], [94LEO/SEP]

- 3. Comment/formation without characterization -[87ALL/POL]
- 4. Patent (lubricants) -[84STE]

The status of the characterization of solid Br2O3 is best summarized by statements provided by Allen et al. [87ALL/ POL]: "There has also been considerable work on the vibrational spectra of the solid higher oxides of bromine (Br₂O₃, Br₂O₄), but structural conclusions had to be somewhat tentative." Pascal et al. [74PAS/PAV] prepared Br₂O₃ by the thermal decomposition of Br_2O_4 . The authors stated that the vibrational spectrum of Br2O3 shows the presence of a BrOBr bond, but that it was not possible to distinguish between structural possibilities: OBrOBrO and BrOBrO2. Chemical analysis established the stoichiometry. Br₂O₃ was said to be a stable intermediate in the decomposition of Br₂O₄ to Br₂O. A subsequent study [76PAS/PAV], using Raman spectra, indicated that the structure was OBrOBrO. At a conference, these same authors [77PAS/PAV] summarized their work by discussing the synthesis of the two isomers of Br₂O₄, Br₂O₃, and Br₂O in a Raman tube and the spectra obtained at 93 K. The stepwise decomposition of Br₂O₄ to Br₂O was presented and vibrational frequencies assigned. In summary, analysis of the vibrational spectra of the crystalline phase by Pascal et al. [76PAS/PAV, 77PAS/PAV] of the various possible isomers of Br₂O₃ and Br₂O₄, suggested that Br_2O_3 has the structure (OBrOBrO) and that the two Br_2O_4 isomers have the structure (O₂BrBrO₂) and (O₂BrOBrO).

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

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

5.10. BrOBrO₂ ($Br^+BrO_3^-$)

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

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

5.11. Br_2O_4 (O_2BrBrO_2)

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

- 1. Formation and characterization -
 - [73PAS/POT], [74PAS/PAV], [76PAS/PAV], [77PAS/PAV], [87ALL/POL], [94LEO/SEP]
- 2. Intermediate in solution -

[80FOE/LAN], [83FIE/RAG], [91SZA/WOJ].

Pascal and Potier [73PAS/POT] interpreted the Raman spectrum of the BrO₂ crystalline form (-180 °C) in terms of a dimeric structure with a Br-Br bond. They specifically ruled out a chain or ring structure with bridging oxygen atoms. Tentative assignments were made for some of the observed frequencies. In a subsequent study [74PAS/PAV] of the vibrational spectra of Br₂O₃, the authors discussed the corresponding spectra of Br₂O₄ and suggested the structure to be O_2BrBrO_2 . In studying the reaction between ozone and Br₂O₃, Pascal et al. [76PAS/PAV, 77PAS/PAV] observed two isomers of Br_2O_4 . The asymmetric isomer [O₂BrOBrO], was not isolated and rapidly transformed to the symmetric isomer [O₂BrBrO₂]. An analysis of the vibrational spectra of the various possible isomers of Br₂O₃ and Br₂O₄ suggested that Br₂O₃ has the structure (OBrOBrO) and that the two Br_2O_4 isomers have the structure (O_2BrBrO_2) and (O ₂BrOBrO). Some tentative spectral assignments have been made. [94LEO/SEP] questioned the existence of this compound.

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

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

- The Belousov-Zhabotinsky-system-(HBrO₂)/BrO₃⁻ reaction [80FOE/LAN],
- (2) The pulse radiolysis of the bromine dioxide radical and hexacyanoferrate (4-), manganese (II), phenoxide ion, or phenol [83FIE/RAG], and
- (3) The pulse radiolysis of the hexacyanoferrate (II)bromate cyanide system in aqueous ethylene glycol [91SZA/WOJ].

5.12. O₂BrOBrO

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

In attempting to study Br_2O , Pascal *et al.* have examined the decomposition of Br_2O_4 and the formation of an intermediate Br_2O_3 . In the analysis of the vibrational spectra of Br_2O_3 , [74PAS/PAV] discussed the corresponding spectra of Br_2O_4 and suggested the structure to be O_2BrBrO_2 . Subsequent studies by Pascal *et al.* [76PAS/PAV, 77PAS/PAV] prepared two isomers of Br_2O_4 . These authors observed a slow reaction between ozone and Br_2O_3 . The asymmetric isomer [O₂BrOBrO] formed was not isolated and rapidly transformed to the symmetric isomer [O₂BrBrO₂]. An analysis of the vibrational spectra of the various possible isomers of Br_2O_3 and Br_2O_4 suggested that Br_2O_3 has the structure (OBrOBrO) and that the two Br_2O_4 isomers have the structure (O₂BrBrO₂) and (O₂BrOBrO). Some tentative spectral assignments have been made. [94LEO/SEP] questioned the existence of this compound.

5.13. BrBrO₄

Gilson *et al.* [92GIL/LEV] discussed the formation of BrBrO₄ by passing a mixture of bromine and oxygen through a discharge tube. The authors were surprised that with the hydrolysis of the yellow solid, BrO_4^- was identified in the solution. Bromine K-edge EXFAS data on this solid detected vibrations which were assignable to a Br-O-Br bridge. This is in contrast to the results of [73PAS/POT]. Three distinct shells were observed corresponding to terminal Br-O, bridging Br-O, and nonbonded Br-Br distances at 1.61(2), 1.86(2), and 3.05(3) Å respectively, concomitant with the proposed structure. A Br-O-Br bridging angle of $110\pm 3^{\circ}$ was calculated by triangulation. [94LEO/SEP] supported the existence of this isomer.

5.14. Br₂O₅

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

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

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

Pascal *et al.* [76PAS/PAV2] recorded the Raman spectra of the white solid Br_2O_5 . The authors deduced that the structure ($O_2BrOBrO_2$) was a symmetric, polymeric structure similar to I_2O_5 . Comparison of the observed Raman spectra with that known for the ions bromite, bromate and perbromate resulted in the identification of vibrations which were

attributed to a bromine-terminal oxygen and a -bridging oxygen. Additional assignments were presented by the authors to justify their selection of the structure. In a later study, [77PAS/PAV] suggested that in the reaction of ozone with bromine, whenever Br_2O_5 was formed, it was always mixed with Br_2O_3 or Br_2O_4 . The authors continued to propose a polymeric structure (for Br_2O_5) analogous to that of I_2O_5 .

Leopold and Scppelt [94LEO/SEP] presented a crystal structure analysis which characterized Br_2O_5 which crystallized with three molecule propionitrile. The structure was depicted as $O_2BtOBrO_2$. The Raman spectra of solvate-free Br_2O_5 was in agreement with this structure. The Raman spectra determined by [94LEO/SEP] differs from that by [76PAS/PAV2].

5.15. Br₂O₆

The available information does not conclusively confirm the existence of Br_2O_6 . The nine articles listed in the bibliography refer to the preparation of the condensed phase oxide Br_2O_6 (or BrO₃). All articles involved the reaction of ozone with bromine, except Mungen and Spinks [40MUN/ SPI] who were actually investigating the decomposition of ozone. No property data have been reported. There is no gas phase information.

Schwarz and Wiele [38SCH/WIE] studied the thermal decomposition of BrO₂. In addition to the formation of the elements, the authors also detected a white oxide which they presumed was Br₂O₇ or Br₂O₆ and a dark-brown oxide, Br₂O. Schwarz and Wiele [39SCH/WIE] continued their study of the thermal decomposition of BrO₂. Their study showed that BrO₂ is completely stable at -40 °C, but that decomposition can be detected manometrically. BrO₂ sublimes with extensive decomposition, melting in dry air at approximately -17.5 °C. Br₂O is stable at -40 °C. Again Br₂O₇ was suggested as one of the decomposition products of BrO₂.

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

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

5.16. Br₂O₇

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

Schwarz and Wiele [38SCH/WIE] studied the thermal de-

composition of BrO_2 . In addition to the formation of the elements, the authors also detected a white oxide which they presumed was Br_2O_7 or Br_2O_6 and a dark-brown oxide, Br_2O . Schwarz and Wiele [39SCH/WIE] continued their study of the thermal decomposition of BrO_2 . Their study showed that BrO_2 is completely stable at -40 °C, but that decomposition can be detected manometrically. BrO_2 sub-limes with extensive decomposition (to Br_2), melting in dry air at approximately -17.5 °C. Br_2O is stable at -40 °C. Again Br_2O_7 was suggested as one of the intermediate decomposition products of BrO_2 . According to Pflugmacher [55 PFL, S5PFL/RAB], Br_2O_7 probably did not exist.

5.17. Br₃O₈

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

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

All citations can be grouped into five categories.

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1. Patent -
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[90JOO] and [91BEN/GER]

[89BRU/AND], [89CAR/SAN], [90BOT/BAR], and [91MOU/JAK]

[34BRA], [60GEO], [63SCH/BRA]

- 4. Formation/preparation/decomposition -
- [28LEW/SCH], [29LEW/SCH],[29LEW/SCH2], [30LEW/SCH], [55PFL], [55PFL/RAB], [58ARV/ AYM], [59ARV/AYM], [59PFL], [59SCH], [74SOL/ KEI]
- 5. Sensitized decomposition of ozone [31LEW/FEI], [31SPI], [40MUN/SPI].
- 6. Reaction -
 - [90BIG/BRO]

When Lewis and Schumacher [28LEW/SCH] allowed bromine and ozone to mix in a flask (no temperature was specified), a white deposit appeared on the walls on the flask. This solid was thought to be an oxide of bromine, later described as Br_3O_8 . Shortly after the formation of the solid, an explosion destroyed the apparatus. In subsequent work by Lewis and Schumacher [29LEW/SCH] at low temperatures, -5 to 10 °C, an oxide of bromine was formed which had the composition Br_3O_8 and existed in two crystalline modifica-

^{2.} Misclassified as Br₃O₈ (really BrO) -

^{3.} Review -

tions. Two subsequent studies by the same authors [29LEW/ SCH, 29LEW/SCH2] examined the thermal reaction in more detail to observe the formation and the rate of decomposition. The transition temperature between the two presumed crystalline forms was determined to be -35 ± 3 °C. The thermal reaction between bromine and ozone was studied again in 1930 [30LEW/SCH] to determine the kinetics of decomposition.

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

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

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

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

6. NIST JANAF Thermochemical Tables

NIST-JANAF Thermochemical Tables for BrO(g) (Sec. 6.1), $OB_1O(g)$ (Sec. 6.2), $B_1OO(g)$ (Sec. 6.3), $B_1O_3(g)$ (Sec. 6.4), BrOBr(g) (Sec. 6.5), and BrBrO(g) (Sec. 6.6) are presented on the following pages.

Bromine Oxide (BrO)

Br₁O₁(g) = 0.1 MPa

NIST-JANAF THERMOCHEMICAL TABLES

FOR THE

BROMINE OXIDES

1093

6 = 19332 °(298.151	: ± 200 cm ⁺ \$) = 232.97 ±	: 0.1 J K ⁻¹ -me	1				$\Delta_{\rm f} H^{\circ}($ $\Delta_{\rm f} H^{\circ}(298.1)$	0 K) = 133.3 ± 5 K) = 125.8 ±	2.4 kJ·mol ⁻¹ 2.4 kJ·mol ⁻¹	Enthalpy	Reference	Temperatur J·K ⁻¹ mol	e = T _r = 298.15	к <u> </u>	standari Stat _kJ·mo⊡'	e Pressure =	p°
										<i>Т /</i> К	C,°	S° −[G°− <i>H</i> *(T _r)]/T	$H^{\circ} - H^{\circ}(T_{r})$	$\Delta_{\rm f} H^{\circ}$	$\Delta_{c}G^{\circ}$	
State	L	<i>K</i> ,	ω,.	Electroni @eXe	c Levels and M	Molecular Cons Be	tants (⁷⁹ Br ¹⁶ O), c	$m^{-1} D_{e} = 10^{6}$	r./Å	0 50	0.0	0.0 179.334	INFINITE 331.631	~9.061 -7.615	133.305 133.611	133.305 129.149	IJ
$\begin{array}{c} X^2 \Pi_{3/2} \\ X^2 \Pi_{1/2} \end{array}$	0 968	2 2	727.05 727.05	4.932	-	0.4299	0.003639	0.594 0.594	1.717	100 150 200 250	29.139 29.592 30.805 32.493	199.511 211.388 220.050 227.101	261.104 242.681 235.985 233.523	-6.159 -4.694 -3.187 -1.606	133.358 132.932 132.424 131.859	124.765 120.555 116.505 112.588	
$A^2 \Pi_{1/2}$ $A^2 \Pi_{1/2}$	27871 [29321]	22	511.3 511.3	4.83 4.8	-0.074 -0.074	0.314 0.314	0.0034 0.0034	0.474 0.474	1.95 1.95	298,15 300 400 500	34.182 34.244 37.062	232.970 233.182 243.447 251.015	232.970 232.971 234.351 237.042	0.000 0.063 3.638 7.436	125,770 125,736 110,536	109.582 109.482 107.200	
nthalpy of The two tould not irge-Spor	of Formation existing spect existing response to extrapolation of the ex	roscopic studie of to those studie on of the Colo ion was high h	s by Ccleman dies, that the man and Gayd	and Gayde first boun lon ¹ data g	on ¹ and Durie a d excited state ave 17800 cm ² amended 1.75	nd Ramsay ² yie A ² II of BrO(¹ or 213.2 kJ n + 0.3 eV or 17	eld dissociation er g) dissociates to nol^{-1} for the grou 0 + 29 k 1 mol ⁻¹	hergy values fo Br($^{2}P_{3/2}$) + O(and state dissoc	r BrO(g). One ${}^{1}D_{2}$). A linear siation energy. msay 2 from a	600 700 800 900 1000	39.525 39.839 39.901 39.846 39.746 39.634	259.055 265.176 270.502 275.199 279.392 283.175	240.132 243.283 246.360 249.308 252.111 254.766	11.354 15.325 19.313 23.301 27.281 31.250	111.486 111.950 112.405 112.808 113.170 113.493	105.307 105.321 104.256 103.125 101.940 100.713 99.451	

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State	T _c	81	ω _e	Electronic ω _e x _e	Levels and M ω _e y _e	Aolecular Constan	nts (⁷⁹ Br ¹⁶ O), cn α_c	$n^{-1} D_{e} - 10^{6}$	r./Å	0 50 100	0,0 29,103 29,139	0.0 179.334 199.511	INFINITE 331.631 261.104	9.061 7.615 6.159	133.3)5 133.611 133.358	133.305 129.149 124.765	INFINITE 134.918 65.169
$X^2 H_{12}$	0	2	127.05	4.932	-	0.4299	0.003639	0.594	1.717	150	29.592 30.805	211.388 220.050	242.681	-4.694 -3.187	132.932	120.555	-41.980 -30.427
$X^{2}H_{1,2}$	968	2	727.05	4.932	-	0.4299	0.003639	0.594	1.717	250	32.493	227.101	233.523	-1.606	131.859	112.588	-23.523
A*IL:2	27871	2	511.3	4.83	-0.074	0.314	0.0034	0.474	1.95	298.15	34.182	232.970	232.970	0.000	125,770	109.582	- 19,198
A 111/2	[27.121]	-	211.2	4.0	0.074	014	0.00.04	0.4/4	1.95	300 400	34.244 37.062	233,182 243,447	232.971 234.351	0.063	125.756	109.482	- 19.062 - 13.999
				Point Gro	up: C _{av}			σ=1		500	38,719	251.915	237.042	7.436	111.008	106.307	-11.105
Enthalov o	of Formation									600 700	39.525 39.839	259.055 265.176	240.132 243.283	11.354 15.325	111.486 111.950	105.321 104.256	-9.169 -7.780
The two e	existing spect	roscopic studies	by Ccleman	and Gaydo	n ¹ and Durie a	nd Ramsay ² yield	dissociation en	ergy values fo	or BrO(g). One	800	39.901	270.502	246.360	19.313	112.4)5	103.125	-6.733
should note Birge=Spon	e, with respo per extranolati	ct to those studi	es, that the an and Gave	first bound	excited state	A ⁻ 11 of BrO(g)	dissociates to	$Br(^{4}P_{3/2}) + Or nd state disso$	(¹ D ₂). A linear	1000	39.746	279.392	252.111	27.281	113.170	100.713	-5.261
Assuming t	he extrapolat	ion was high by	up to 20%.	they recom	mended 1.75	± 0.3 eV or 170	$\pm 29 \text{ kJ} \text{ mol}^{-1}$	Durie and Ra	amsay, ² from a	1100	39.634	283.175	254.766	31.250	113.493	99.451	-4.722
graphical B	irge-Sponer of	extrapolation, ca	culated a di	ssociation en	nergy of $D_0^\circ =$	$19332 \pm 200 \text{ cm}$	or 231.6 \pm 2.	4 kJ·mol ⁻¹ . 1	The latter value	1300	39.437	289.779	259.659	39.156	114.036	96.850	-3.891
presented h	ere, e.g. then	mal functions fo	r the Br(g),	and Br ₂ (ref	O(g) O(g), and C	(ref), are taken	from the JANA	F Thermoche	emical Tables.	1400	39.361 39.301	292.699 295.412	261.916 264.060	43.096 47.029	114.265	95.519 94 173	-3.564
										1600	39.256	297.947	266.099	50.957	114.647	92.814	-3.030
The speci	troscopic resi	a ropy ults tabulated ab	we are for t	he ⁷⁹ Br ¹⁶ O i	isotopomer. Is	otonic relationshi	ips ⁴ are used to	convert the a	bove constants	1700	39.225 39.2 05	300,326 302,568	268.043	54.881 58.802	114.805	91.445 90.066	-2.810 -2.614
to those for	the normally	occurring, i.e. na	itural ibunda	ince, specie	s. The latter va	lues are then use	d in the calculati	ion of the the	rmal functions.	19()0	39.194	304.687	271.675	62.722	115.057	88.681	-2,438
Only the X Values of	and A states	are included in	the calculati	on of the th	tate are from	ns; a sum-over-s	tates technique	is used.	l state are from	2100	39,189	308.609	275.009	70.560	115.05	85 895	-2.136
Barnett et a.	1.6 These val	lues in fact descr	ibed an avera	age ² H state	; there are diff	erences in the vit	prational constan	ats for the X ²	$\Pi_{3/2}$ and $X^2 \Pi_{1/2}$	2200	39.189	310.432	276.578	74.479	115.279	84.497	-2.006
states but the	iey are not co	onsidered in this	calculation.	The B _e valu	ie for the grou	nd state is from A	Amano et al.' T	he internucle	ar distance and	2400	39.182	313.842	279.544	82.316	115.318	81.697	-1.778
energy of 8	$960 \text{ cm}^{-1} \text{ for}$	the A state which	th is used in	conjunction	$D_{\rm e}$ for the ex-	ovide an energy	cutoff from the	sum-over-sta	tes calculation	2500	39.168	315.441	280.948	86.234	115.303	80.296	- 1.678
on the excit	ted state.	e.a		e a de las		V2T1 1				2700	39.145	318.454	282.504 283.616	94.062	115.204	77.498	-1.585
average has	ly, the value sed on two va	of the spin orbit dues derived fro	constant, A, m the EPR :	spectra stud	lies: $A_{-} = -81$	5 cm of Carrin	e adopted by H	$A_{\mu} = -980 c$	rzberg" was an	2800 2900	39.061 38.996	319.875 321.245	284.886	97.971 101.874	115.112	76.103 74.711	-1.420
et al. ¹⁶ The	recent measu	ired value of Mc	Kellai, ¹¹ A.,	= -968 cm	1, for the spin	n-orbit splitting of	of the ground sta	ite is adopted	here. For ClO	3000	38.915	322.566	217.309	105.770	114.858	73.325	-1.277
the spin-ort	bit splitting c	of the A state is	approximate	ly 1.5 times d to be 145	s the value for 50 cm^{-1}	and for the groun	id state.12 Using	the same fac	ctor of 1.5, the	3100 3200	38.817 38.701	323.840 325.071	288.467	109.656	114.690	71.945 70.568	-1.212
Numerou	is excited sta	tes have been es	timated by	Monks et a	1.13 and obser	ved by Duignan	and Hudgens.14	These state	s are not fully	3300	38.568	326.260	290.685	117.396	114.276	69.198	-1.095
characterize	ed in terms o	f vibrational and	rotational of	onstants an	nd do not com	ribute significant	ly to the therm	al functions	below 6000 K.	3,500	38.251	328.520	292.783	125.079	113.755	66.483	-0.992
References										3600	38.068	329.595	293.791	128.895	113.453	65.136	-0.945
E. H. Cole	man and A.	G. Gaydon, Disc	ussions Fara	day Soc. (2	.), 166 (1947).					3800	37.661	331.643	294.773	136.469	112.769	62.471	-0.859
TANAF Th	e and D. A. I hermochemic:	amsay, Can. J. al Tables: Br(9).	Phys. 36 , 33 June 1982	5 (1958). Br5(ref), Jui	ne 1982: O(g)	Sept 1982 Ost	ref), Sept. 1982			3900 4000	37.439 37.205	332.618	296.663 297.574	140.224	112.289	61.150 59.840	-0.819
G. Herzber	rg. Spectra of	Diatomic Mole	cules, D. Va	n Nostrand	Co., New Yo	rk, p. 107 (1950)		•		4100	36.%3	334.479	298.463	147.665	111.547	58,545	-0.746
'J. E. Butler ⁶ M Barnott	r, K. Kawagu	ichi and E. Hirol	a, J. Mol. S way: Cap. 1	pectrosc. 10 Phys 59(1)4 (2), 372–9 (2) 1908–16 (1984).				4200 4300	36.712 36.454	335,366 336,227	299.331 300.179	151.349	111.088	57.255 55.980	-0.712
² T. Amano,	A. Yoshinag	ga and E. Hirota,	J. Mol. Spe	ctrosc. 44(3	33), 594-8 (19	72).				4400	36.191	337.062	301.008	158.639	110.093	54.717	-0.650
⁸ K. P. Hube	er and G. Her	zberg, Molecula	r Spectra an	d Molecular	r Structure, IV	Constants of D	iatomic Molecu	les.		4500	35.654	338 659	302.611	165 824	109.259	53,403 52,222	-0.593
¹⁰ J. M. Broy	wn. C. R. By	fleet, B. J. How	ard, and D. I	K. Russell,	Mol. Phys. 23	(3), 457–68 (197	2).			4700	35.382	339.423	303.386	169.376	108.416	50.994	-0.567
¹¹ A. R. W.	McKellar, J.	Mol. Spectrosc.	86(1) 43-5	4 (1981).	2					4809	34,835	340,165	304.144 304.887	176.397	107.109	49.780 48.579	-0.542
										5000	34.562	341.587	305.614	179.867	106.523	47.388	-0.495
										5100	34.291 34.021	342.269 342.932	306.326 307.024	183.310	105.844	46.213 45.048	-0.473
										5300 5400	33.755	343.578	307.707	190.114	104.418	43.900	-0.433
										5500	33.232	344.818	309.034	196.813	102.898	41.646	-0.396
										5609	32.976	345.415	309.679	200.123	102.103	40.537	-0.378
										5800	32.477	346.563	310.931	206.668	100.444	38.367	-0.346
										5900 6000	32.235 31.998	347.116 347.656	311.540 312.137	209.903	99.579 98.690	37.305	-0.330
															200020		0.010
										PREVIOL	3				<u>C</u> l	UKRENT: Ma	rch 1996 (1 b

Bromine Oxide (BrO)

Ideal Gas

M_r = 111.9028 Bromine oxide (OBrO)

1094

$\Delta_{\mathbf{a}} H^{\alpha}(0 \mathbf{K}) = [450] + 25] \mathbf{k} \cdot \mathbf{m} ^{-1}$	$\Delta_1 H^{\circ}(0 \text{ K}) = \{161.5 \pm 25\} \text{ kJ-mol}^{-1}$	Enthalpy	Reference	Temperature	= 7, = 298.15	к 5	standard Stat	e Pressure =	p° = 0.1 MPa
N (298,15 K) ≈ 271.1 ° 2 J K = (mo)	$\Delta \mu (250.15 \text{ K}) = (152.0 \pm 2.5) \text{ KJ mos}$	ТК	$\overline{C_{p}^{\circ}}$, K mor S° -[($\vec{r}^{\circ} - i \vec{r}^{\circ}(T_{r})] / T_{r}$	$\frac{1}{H^{\circ}-H^{\circ}(T_{r})}$	Δ _r H°	$\Delta_{\rm r}G^\circ$	log K,
Electronic Level and Quantum Weight State ϵ_r , cm $\frac{3}{2}$ g_r X^2B_1 QO 2		0 50 100 150 200 250	.000 33.368 35.399 37.993 40.539 43.088	.000 204,239 227,876 242,726 254,003 263,324	INFINITE 398.861 308.078 283.956 275.111 271.846	-11.395 -9.731 -8.020 -6.185 -4.222 -2.131	161,500 161,299 160,573 159,790 159,010 158,236	161,500 159,420 157,809 156,596 155,649 154,898	INFINITE - 166.544 - 82.431 - 54.531 - 40.651 - 32.364
Vibration:1 Frequencies and Degeneracies v. cm ⁻¹ 800 (1) 300 (1) 852 (1)		298,15 300 400 500 700 800 900	45.364 45.446 49.171 51.674 53.335 54.463 55.253 55.253	271.112 271.393 285.010 296.270 305.848 314.160 321.487 328.030	271.112 271.113 272.944 276.516 280.626 284.836 288.969 292.952	.000 .084 4.826 9.877 15.133 20.526 26.015 31.570	151.957 151.916 136.447 136.594 136.830 137.100 137.375 137.643	154.979 154.998 159.211 164.888 170.525 176.120 181.675	- 27.152 - 26.988 - 20.791 - 17.226 - 14.846 - 13.142 - 11.862 - 10.865
Point Group: C_{2} , Bond Distance, Br. O = 1.649 Å Bond Angle: O-Br. O = 114.4" Product of the Moments of Inertia: $I_{A}t_{B}t_{C}$ = 409.0844 × 10 Enthalpy of Formation	σ = 2) ¹¹⁷ g ¹ cm ⁶	1000 1100 1200 1300 1400 1500	56.246 56.567 56.817 57.013 57.172 57.301	326,050 333,934 339,311 344,244 348,800 353,031 356,980	192.932 196.760 500.387 503.839 507.125 510.254 513.239	37.174 42.816 48.485 54.177 59.887 65.611 71.346	137.898 138.139 138.364 138.364 138.572 138.764 138.937 139.090	197.196 192.688 198.156 203.602 209.030 214.442 219.842 219.842	- 10.865 - 9.410 - 8.863 - 8.399 - 8.001 - 7.656
For the series OXO(g) (where $X = F$, Cl. 3r, U, there is only reliable experimental data 1 $\Delta_{all}^{T'}(OC(O,g))$ and $D_{all}^{*}(Cl)$ are reasonable, we adopt the ratio of the numbers (~1.94) to apply and OBrO(g). Thus we calculate $\Delta_{all}^{T'}(OBrO, g, OK) = 1.94 \times D_{all}^{*}(BrO) = 450 \pm 25 \text{ kJ-mol}^{-1}$. Cottrell ⁴ reported $D(O(BrO) \approx 70 \pm 10 \text{ kcl-mol}^{-1}$. This reoverts to $\Delta_{all}^{T'}(OK) = 87 \text{ kJ-mol}^{-1}$ formation of BrO ₃ (cr) reported by Pflugmacher <i>et al.</i> ² and $a D_{all}^{*}(BrO) = 2.25 \text{ eV}$ or 52 kcl-mol ⁻¹ of this value based on comparison with ClO ₂ . The enthalpy of dissociation reported by Vedeneye	or OCIO(g). Assuming that the values for a similar relationship between BrO(g) ¹ . This value was based on the enthalpy of . Cottrell expressed doubt as to the validity v et al. was $\Delta H(298 \text{ K}) \ge 70 \text{ kcal-mol}^{-1}$	1700 1700 1800 1900 2000 2100 2200 2300	57.407 57.495 57.570 57.634 57.688 57.735 57.776 57.776	360,081 364,164 367,453 370,567 373,525 376,341 379,028	510.090 518.816 521.428 523.933 526.339 528.654 530.883 530.883	71.346 77.091 82.845 88.605 94.371 100.142 105.918	139.090 139.223 139.334 139.420 139.481 139.515 139.520 139.520	225.230 230.610 235.982 241.349 246.712 252.073 257.433 267.433	- 7.353 - 7.086 - 6.848 - 6.635 - 6.443 - 6.270 - 6.112 - 6.112
for the reaction BrO ₂ -BrO ₂ O ₃ (). This is an estimated value based on the work by Cottell (1954) a In contrast, Huie and Laszlo ⁴ have estimated the enthalpy of formation of OBrO(g) in the fold enthalpy of formation of OBrO in the gas phase can be estimated by assuming that the different applies for the bromine species. Using a value of 2.9 kJ mol ⁻¹ recommended by Wagman <i>et al.</i> ⁶ a kJ-mol ⁻¹ , we obtain $\Delta G'' = 146.9$ kJ-mol ⁻¹ for OBrO(g) and $\Delta_d H'' = 122.5$ kJ-mol ⁻¹ . In compar	iffhough a different temperature was given. wing manner. According to Stanbury, the ce in the Δ_{fG} for Cl ₂ (g) and ClO ₂ (aq) also s this difference and Δ_{G} (BrO ₂ , aq) = 144.0 ison D_{c}^{c} (BrO) = 231.6 kJ·mol ⁻¹ .	2400 2500 2600 2700 2800 2900 3000	57.843 57.843 57.871 57.896 57.918 57.937 57.955 57.971	384.058 386.420 388.690 390.875 392.982 395.015 396.980	135.108 135.108 137.113 139.053 140.933 140.933 142.754 144.521 146.237	111.096 117.480 123.266 129.054 134.845 140.638 146.433 152.229	139,443 139,358 139,244 139,100 138,926 138,725 138,496	262.792 268.154 273.519 278.887 284.261 289.640 295.026 300.420	-5.836 -5.715 -5.603 -5.499 -5.403 -5.314 -5.314
Heat Capacity and Entropy MacIler et al. ¹ have measured the microwave spectra of O3rO(g). Preliminary analysis of the Å and $<$ (OBrO) = 114.4"). This structure is adopted and is consistent with the expected trends in the molecules. The principal moments of inertia (in g cm ²) are: $i_A = 3.0275 \times 10^{-19}$, $I_B = 10.2087 \times$ In support of this study. Byberg and Spanget-Larsen ⁴ used modified extended Huckel theory constants for a series of oxygen halogen compounds. The comparison of calculated values with ob of BrO ₂ : C_{25} symmetry with a bond length of 1.625 Å and a bond angle of 117.6". This geometry using a 0.15 Å difference between the covalent radii of the chlorine and bromine atoms. Tevault et al. ⁴ observed the infrared spectra of BrO ₂ in a solid argon matrix. Assuming the transition is the spectra of the wave male wave calculated to be 1.10 ± 2°. This was close to the	data suggested a bent structure ($r_0 = 1.649$ he corresponding chlorine and iodine oxide (10^{-19} , and $I_c = 13.2361 \times 10^{-19}$. to calculate nuclear quadrupole coupling served values helped confirm the geometry was assumed to be similar to that of ClO ₂ , proper identification of the antisymmetric to value observed for the analogous matrix	3100 3200 3300 3400 3500 3600 3700 3800 3900 4000	57.986 57.999 58.011 58.022 58.032 58.041 58.050 58.058 58.065 58.065	398,881 400,723 402,508 404,240 405,922 407,557 409,147 410,695 412,203 413,673	147.905 349.527 351.106 352.643 354.141 355.602 357.028 358.420 359.780 361.109	158.027 163.826 169.626 175.428 181.231 187.035 192.839 198.644 204.451 210.257	138,243 137,965 137,666 137,347 137,010 136,657 136,289 135,908 135,517 135,116	305.822 311.231 316.650 322.079 327.517 332.965 338.423 343.892 349.370	-5.153 -5.080 -5.012 -4.948 -4.888 -4.888 -4.831 -4.778 -4.777 -4.679
Subtracting P_{1} is the 5/2 cm ⁻¹ the appendix large that characterize to $E = 10^{-1} D_{12}^{-1} M_{13}^{-1}$ mass that we do insolated CO ₂ . The recommended vibrational frequency (ν_{i}) is that suggested by Jacox. ³⁰ This data is based of isolated radia at as tudied by Tevault <i>et al.</i> ² Peliminary microwave studies by Mueller <i>et al.</i> ² sis cm ⁻¹). The unobserved vibrational frequency (ν_{i}) is estimated from those which describe the of Bothur, ²¹ using flash photolysis, trapped OBrO in a matrix and measured ν_{i} and ν_{i} for two isotope numbers of the values derived by Tevault <i>et al.</i> ⁹ ν_{i} values are of the order of 791–799 cm ⁻¹ , depe mixture (Br ₂ /O ₂ /Ar).	on the infrared spectra of the argon matrix uggested an approximate value for v_2 (300 ther halogen oxide molecules. ¹¹ Maier and s. Their values for v_1 are within a few wave nding on the concentration of the pyrolized	4100 4200 4300 4400 4500 4600 4700 4800 4900	58.072 58.078 58.084 58.089 58.094 58.099 58.103 58.107 58.111 58.115	415.107 416.507 417.874 419.209 420.515 421.792 423.042 424.265 425.463	362.409 363.680 364.925 366.143 367.337 368.507 369.654 370.779 371.883	216.065 221.873 227.682 233.491 239.300 245.111 250.921 256.732 262.543	133.110 134.707 134.291 133.870 133.444 133.014 132.581 132.145 131.707 131.266	360,357 365,866 371,385 376,913 382,451 387,998 393,556 399,122 404 698	-4.534 -4.591 -4.550 -4.511 -4.475 -4.439 -4.406 -4.374 -4.343 -4.314
 References ¹T. L. Cottrell, The Strengths of Chemical Bonds, Butterworths, London, 221–81 (1954). ¹A. Pflugmacher, R. Schwarz and H. J. Rabbin, Z. anorg, u. allgem, Chem 264, 204–8 (1951). ¹V. I. Vedeneyev, L. V. Gurvich, V. N. Koncrat'yev, V. A. Medvedev and Ye, L. Frankevich Electron Affinities, Arnold, London, 78–130 (1966). ⁴R. Huie and B. Laszlo, Adv. Chem. Series: in press (1995). ⁵D. M. Stanburry, Adv. Inorg. Chem. 33, 69–138 (1989). ⁶D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, and S. M. Bailey, NBS- ⁷H, S. P. Mueller, C. Miller and E. A. Cohen, submitted for publication in Angew. Chem. ⁸J. R. Byberg and J. Spanget-Larsen, Chem. Phys. Lett. 23(2), 247 (1973). 	, Bond Energies, Ionization potentials and -TN-270-3, 31 (1968).	5000 5100 5200 5300 5400 5500 5500 5700 5700 5800 5800 5900 6000	58,118 58,121 58,125 58,127 58,130 58,133 58,133 58,133 58,137 58,140 58,142 58,144	426.637 427.788 428.917 430.024 431.111 432.177 433.225 434.254 435.265 436.259 437.236	372,966 374,030 375,075 376,101 377,110 378,101 379,076 380,035 380,979 381,907 382,821	268.355 274.167 279.979 285.792 291.605 297.418 303.231 309.045 314.859 320.673 326.487	130.823 130.377 129.928 129.475 129.018 128.557 128.089 127.615 127.134 126.644 126.143	410.283 415.877 421.479 427.091 432.710 438.338 443.975 449.620 455.273 460.934 466.605	-4.286 -4.259 -4.234 -4.209 -4.186 -4.163 -4.163 -4.141 -4.120 -4.100 -4.081 -4.062
 ⁹D. E. Tevault, N. Walker, R. R. Smardzewski, and W. B. Fox, J. Phys. Chem. 82, 2733 (1978). ¹⁹M. E. Jacox, J. Phys. Chem. Ref. Data, Monograph No. 3, 461 pp. (1994). ¹⁹JANAF Thermochemical Tables: OCIO(g): Sept. 1995; OIO: Sept. 1995.).	PREVIOU	5:	<u> </u>			CL	JRRENT: Ma	ch 1996 (1 bar)
¹² G. Maier and A. Bothur, Z. anorg. allg. Chem. 621 , 743–45 (1995).		Bromin	e oxide	(OBrO)					Br ₂ O ₂ (a)

Bromine Oxide (OBrO)

MALCOLM W. CHASE

) (L BrO)

Bromodioxy (BrOO)	Ideal Gas	<i>M</i> _r = 111.9028	Bromine	e Oxide	(BrOO)					Br₁O₂(g
$S''(298.15 \text{ K}) = 1288.8 \pm 31.1 \text{ K}^{-1} \text{ mol}$	11	$\Delta_1 H^{\circ}(0 \text{ K}) = [116.1 \pm 40] \text{ kJ} \cdot \text{mol}^{-1}$ $\Delta_2 H^{\circ}(298.15 \text{ K}) = [108.0 \pm 40] \text{ kJ} \cdot \text{mol}^{-1}$	Enthalpy	Reference	Temperatu	re = T _r = 298.15 K		Standard Sta	te Pressure =	p° = 0.1 MPa
		$\Delta \mu = (2.0.15 \text{ K}) = (100.0 \pm 40) KJ more$	ТЛК	C _p °	j.K mo	$[G^{\circ}-H^{\bullet}(T_{r})]/T$	$H^{\circ}-H^{\circ}(T_{r})$	ΚJ*moi Δ _f H°	Δ _r G°	$\log K_t$
	Electronic Level and Quantum Weight		C 50	.000 35,382 41,818	.000 212.021 238.630	INFINITE 435.344 330.008	-12.851	116.087	116.087 113.639	INFINITE -118.718 -58.278
	$\frac{1}{ \mathbf{x} ^2 \mathbf{A}'' } = \frac{1}{ 0,0 } = \frac{1}{ 0,0 } = \frac{1}{ 0,0 }$		150	45.376	256.347	303.261	-7.037 -4.720	114.981	109.743	-38.216
			250	48.143	280,301	289.646	-2.336	114.073	106.491	~ 22.250
	Vibrational Frequencies and Degeneracies		300	48,875	288.845	288,845	.000	108,000	105.736	~ 18,524
	ν, cm ⁻¹		400	50.265 51.562	303.404	290,781	5.049	92.714	108.119	-14.119
	1487 (1)		600	52.707	324.266	298.672	15.356	93.097	115.741	- 10.076
	[160] (1)		800	54.421	339.682	307.080	26.082	93.435	123,230	-8.046
	Point Graup: C	$\sigma = 1$	900 1000	55.031	346.128 351.952	311.067 314.869	31.555 37.084	93.671 93.851	126.936	-7.367 -6.823
	Bond Distances: Br–O = $[2.0]$ Å; O–O = $[1.25]$ Å		1100	55.907 56.222	357.263	318.485	42.656	94.022	134.292	-6.377
	Bond Angle: Br-O-O = $[115]^{\circ}$ Product of the Moments of Inertia: $I_A I_B I_C = [588.4497 \times$	(10^{-117}) g ³ cm ⁶	1300	56.480	366.652	325.192	53.898	94.336	141.586	-5.689
		18	1400	56.692 56,869	370.845 374.763	328.305 331.273	59.557 65.235	94.477 94.6)5	145.215	-5.418 -5.183
nthalpy of Formation			1600	57.017 57.142	378.438	334.107	70.930	94.717	152.446	-4.977
Ip and Burns' determined the recom	ibination rate constants of bromine atoms in the presence	e of six different third bodies (helium, neon,	1800	57.249	385.168	339.414	82.358	94.870	159.651	-4.633
id Wood ² and Strong <i>et al.</i> ³ Based on	these data, Blake <i>et al.</i> ⁴ calculated interaction potentials	between atomic bromine, oxygen and an inert	1900 2000	57.341	388.266 391.209	341.904 344.296	88.087 93.825	94.946 94.979	163,247 166,841	-4.488
ird body (such as a rare gas). A value	is giver for Br-O ₂ . BrOO was thought to be unstable w	ith a bond energy (Br-OO) of approximately	2100	57.490 57.550	394.012	346.597	99.571	94.937	170.434	-4.239
\mathbf{K} (at 296.15 K) which trai	istated to an entinality of formation of 108.0 kJ mol ⁻¹ .		2300	57.603	399.247	350,951	111.081	94.923	177.622	-4.034
eat Capacity and Entropy	must an af this must have be been to it is the Dr. O. O. and	of [115] ⁹ and [1] bland (D. O. 12.0]	2400 2500	57.650 57.692	401.700 404.054	353.015 355.010	116.843 122.611	94.849 94.746	181.219 184.820	-3.944
and $r(O-O) = [1.25]$ A. Butkovskay	ya <i>et al</i> , assumed this structure in an attempt to explain	the formation of BrO_2 from the reaction of	2600 2700	57.729 57.763	406.318	356.940	128.382	94.614	188.425	-3.786
+ Br ₂ in a flow discharge system. Un	ider the experimental conditions studied, OBrO was actual $L = 1215117 \times 10^{-19}$ and $L = 1227428 \times 10^{-39}$	ally formed. The principal moments of inertia	2800	57.792	410.598	360.622	139,934	94.256	192.050	-3.650
The recommended vibrational frequ	ency for v_1 is that suggested by Jacox. ⁶ In addition, we	adopt $v_2 = [250]$ and $v_3 = [150]$ cm ⁻¹ based on	2900 3000	57.819 57.844	412.627 414.587	362,380 364,088	145.715 151.498	94.050 93.809	199.278 202.911	-3.589
) assumed trend of the FOO(g) and C is studied by Tevault and Smardzewski	$IOO(g)$ vibrational frequencies. v_1 is based on the infrare	ed spectra of the argon mairix isolated radical	3100	57.866 57.886	416.484	365.748	157.283	93.543 93.254	206.553	-3.480
in conflict with the observed frequer	icy by Tevault and Smardzewski ⁸ and the corresponding	value for ClOO, FOO(g) and ClOO(g) have	3300	57.905	420.104	368.934	168.861	92.944	213.861	-3.385
(O–O stretch) values of 11487 and 14 e bending frequency of 100 cm ⁻¹ wa	4.3 cm ', respectively.' Thus, v_1 =1487 cm ⁻¹ for BrOO ap as consistent with their kinetic data. The recent study by	pears reasonable. The autoors suggested that Majer and Bothur ¹⁰ suggested a us value in	3400 3500	57.922	421.832 423.512	370.464 371.956	174.652 180.445	92.614 92.257	217.531 221.209	-3.342
greement with the adopted value.	the forein and the second state of the forein and the second state of	maler and Bollin Suggested a VI value in	3600 3700	57.951 57.965	425.144 426.732	373.411 374.831	186.239 192.035	91.905 91.528	224.899 228 598	-3.263
eferences			3800	57.977	428.278	376.217	197.832	91.139	232.308	-3.193
. K. K. Ip and G. Burns, J. Chem. P	hys. 51, 3414 (1969).		3900 4000	57.988 57.998	429.784 431.252	377.571 378.895	203.630 209.430	90.740 90.331	236.028 239.759	-3.161 -3.131
& L. Strong, J. W. Chien, P. E. Graf	ans. Raraday Soc. 32, 907 (1936).		4100 4200	58.008 58.017	432.685 434.083	380.189 381.456	215.230 221.031	89.915 89.493	243,499 247,250	-3.102
D. A. Blake, R. J. Browne, and G. Bi	urns, J. Chem. Phys. 53, 3320 (1970).	P21	4300	58.025	435.448	382.696	226.833	89.055	251.012	-3.049
M. E. Jacox, J. Fhys. Chem. Ref. Dat	a, Monograph No. 3, 461 pp. (1994).	65).	4400	58.035	436.782 438.086	385.099	232.636 238.440	88,633 88,197	254,783 258,563	-3.025
ANAF Thermochemical Tables: FO	D(g), Sept. 1995; ClOO(g), Sept. 1995.		4600 4700	58.047 58.054	439.362 440.610	386.265 387.408	244.244 250.049	87.759 87.317	262.354 266.154	-2.979 -2.958
. V. Michael and W. A. Payne, Int. 3	J. Chem. Kinet. 11, 799 (1979).		4800	58,060	441.833	388,529	255.855	86.874	269.964	-2.938
			5000	58.071	443.030	350.709	261.661	86.428 85.979	273.784 277.612	-2.919
			5100 5200	58.076 58.081	445.353 446.481	391.769 392.811	273.276 279.083	85.529 85.075	281.449 285.294	-2.883 -2.866
			5300	58.085	447.587	353.834	284.892	84.618	289.150	-2.850
			5500	58.093	446.673	355.828	290.700	84.157 83.692	293.013 296.884	-2.834
			5600	58.101	450.786 451.814	356.800 357.756	302.319 308.129	83.220 82.743	300.766 304.654	-2.805 -2.792
			5800	58.104	452.824	358.697	313.939	82.258	308.552	-2.779
			6000	58.107	453,818 454,794	359.623 4(0,534	319.750 325.561	81.754 81.250	312.457 316.372	-2.766 -2.754
			PREVIOL	US:				C	URRENT: Mar	<u>ch 1996 (1 ba</u>
			Deserto		. (0					
			Bromin		s (BLOO)					Br₁O₂(

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NIST-JANAF THERMOCHEMICAL TABLES FOR THE BROMINE OXIDES

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$\Delta_a H^o(298.15 \text{ K}) = [625 \pm 50] \text{ kJ} \cdot \text{mol}^{-1}$ $S^o(298.15 \text{ K}) = [284.5 \pm 2] \text{ J} \text{ K}^{-1} \cdot \text{mol}^{-1}$		
	Electroni	c Level and Quantum Weight ϵ_{i} , cm ⁻¹
	$[^2A_1]$	0.0

Vibrational Frequencies and Degeneracies v, cm [442](1) [800](1) [350](2) [828](2) Point Group: C_{3v} Bond Distance: Br--O = [1.68]Å

Product of the Momen's of Inertia: $I_A I_B I_C = 2198.7927 \times 10^{-117} \text{ g}^3 \text{ cm}^6$

Ideal Gas

8 [2]

 $\sigma = 3$

Enthalpy of Formation

Bromine Oxide (BrO₃)

We adopt an enthalpy of formation value which is based on an assumed relationship of $\Delta_{ad}H^{\circ}(BrO_{3},g)/3=0.9D_{0}^{\circ}(BrO)$.

Bond Angle: O-Br-O = [89]°

we acopt an entrary or rotation value when is based on an assumed relationship of Δ_{aft} (BrO, gy/3=0.9D/(BrO). An enthalpy of formation value (at 298.15 K) has been reported by Farkas and Klein.¹ This value, 23 kcal-mol⁻¹ (96 kJ-mol⁻¹), was derived from absorption spectra measurements of bromate ions in solutions. There is considerable uncertainty in this value, both in terms of th experimental measurements and the fact that the authors have interchanged BrO₃ and BrO₃⁻. This corresponds to an average bond energy of $254 \text{ kJ} \cdot \text{mol}^{-1}$. In comparison $D_0^{\circ}(\text{BrO}) = 231 \text{ kJ} \cdot \text{mol}^{-1}$.

Heat Capacity and Entropy

Heat Capacity and Entropy The structure of this molecule is estimated to be pyramidal with a O–Br–O angle of [89]° and a bond length of [1.68] Å, in analogy with the corresponding chlorine and iodine oxide molecules. Venkateswarlu and Sundaram,² Venkateswarlu and Rajalakshmi,³ Rao and Santhamma,⁴ Rao,⁵ and Thirugnanasambandam and Mohan° assumed the same structure and bond angle for ClO₃, BrO₃, and IO₃. Using Badgers' rule, the authors examined the relationship between the vibrational frequencies and force constants for the three pyramidal molecules – ClO₃, BrO₃, and IO₃. Using Badgers' rule, the authors examined the relationship between the vibrational frequencies, the values appear to be in part, those of the ion BrO₄⁻¹. The vibrational frequencies are derived from the force constants which describe the other halogen oxide molecules. The principal moments of inertia (in g cm²) are: $I_A = 12.2156 \times 10^{-19}$, $I_B = 12.2156 \times 10^{-19}$, and $I_C = 14.7352 \times 10^{-19}$. Byberg,⁷ in an EPR study, suggested the molecule had C₁, symmetry with a bond angle of 112° and bond length of 1.57 Å. In contrast, Begum *et al.*,⁸ in a radiolysis study, suggested a bond length of 114° with C_{3w} symmetry. In calculating atomic phase shifts, Lee and Beni² calculated a bond length of 1.66 Å in solution. In these cases, there is no definitive evidence as to the geometry. Values were suggested which would be consistent with experimental observations.

would be consistent with experimental observations.

References

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 *A. Begunt, S. Subramanuan, and M. C. R. Symons, J. Chem. Soc. 6, 918 (1970).

$\Delta_{\rm f} H^{\circ}(0 \text{ K}) = [233 \pm 50] \text{ kJ} \cdot \text{mol}^{-1}$	Enthalpy	Reference	Temperature	$r = 7_r = 298.15$ I	K S	Standard Sta	te Pressure =	p° = 0.1 MPa
$(298.15 \text{ K}) = [221 \pm 50] \text{ KJ mol}$	ТĸК	C _p °	J·K 'mol S° –[($G^{\circ} - H^{\circ}(T_{r})]/T$	$H^{\circ}-H^{\circ}(T_{r})$	$\Delta_{f}H^{\circ}$	$\Delta_{f}G^{\circ}$	log Kr
	50 190 150 200 250	0.000 33.333 36.646 43.085 49.535 55.297	.000 209.520 233.329 249.376 262.667 274.354	INFINITE 438.271 330.438 300.850 289.684 285.471	- 13.101 - 11.438 - 9.711 - 7.721 - 5.403 - 2.779	233.000 232.073 230.636 229.279 228.126 227.156	233.000 233.759 235.992 238.971 242.381 246.060	INFINITE - 244.206 - 123.269 - 83.217 - 63.303 - 51.411
	298.15 300 400 500	59.999 60.162 67.300 71.849	284.509 284.880 303.241 318.785	284,509 284,510 286,965 291,815	.000 .111 6.511 13.485	220,821 220,781 205,483 206,024	250,432 250,616 263,728 278,233	- 43.875 - 43.636 - 34.439 - 29.067
	600 700 800 900 1000	74,791 76,759 78,125 79,105 79,829	332.164 343.850 354.194 363.456 371.830	297.452 303.263 308.995 314.541 319.858	20,827 28,411 36,159 44,023 51,972	206.767 207.599 208.466 209.340 210.208	292.607 306.849 320.969 334.979 348.892	-25.474 -22.897 -20.957 -19.442 -18.224
= 3 cm ⁶	1100 1200 1300 1400 1500	80.377 80.801 81.136 81.404 81.623	379.465 386.478 392.959 398.982 404.606	324.935 329.775 334.389 338.791 342.993	59.983 68.043 76.140 84.268 92.420	211.065 211.905 212.728 213.530 214.311	362.719 376.469 390.149 403.767 417.327	- 17.224 - 16.387 - 15.676 - 15.065 - 14.533
3^{-1} , $3=0.9D_{0}^{0}$ (BrO). $1 \cdot \text{mol}^{-1}$ (96 kJ·mol ⁻¹), was derived in this value, both in terms of the	1600 1700 1800 1900 2000	81,803 81,953 82,080 82,187 82,279	409.880 414.844 419.532 423.972 428.190	347.010 350.856 354.542 358.080 361.481	100.591 108.779 116.981 125.195 133.418	215.067 215.797 216.498 217.168 217.805	430.837 444.300 457.721 471.104 484.452	14.065 13.652 13.283 12.952 12.653
onds to an average bond energy of	2100 2200 2300 2400 2500	82.358 82.428 82.488 82.541 82.588	432.207 436.040 439.705 443.217 446.587	364.754 367.908 370.951 373.889 376.730	141.650 149.889 158.135 166.387 174.643	218.406 218.971 219.499 219.987 220.436	497.770 511.060 524.324 537.566 550.790	- 12.381 - 12.134 - 11.908 - 11.700 - 11.508
and Rajalakshmi, ³ Rao and San- O ₃ , BrO ₃ , and IO ₃ . Using Badgers ³ three pyrantidal molecules – CIO ₃ , dues appear to be in part, those of her balogen oxide molecules. The	2000 2700 2800 2900 3000	82.630 82.667 82.700 82.730 82.757	449.827 452.947 455.954 458.856 461.661 464.375	379,480 382,143 384,726 387,232 389,667	182.904 191.169 199.437 207.709 215.983	220,846 221,217 221,551 221,847 222,108	503.996 577.187 590.365 603.531 616.688	- 11.331 - 11.166 - 11.013 - 10.871 - 10.737
25×10^{-5} ond length of 1.57 Å. In contrast, atomic phase shifts, Lee and Beni ⁹ etry. Values were suggested which	3200 3300 3400 3500	82.804 82.824 82.843 82.843 82.859	464.373 467.004 469.552 472.025 474.427 476.761	392.035 394.335 396.576 398.759 400.887	224,260 232,539 240,821 249,104 257,389	222.536 222.532 222.698 222.837 222.950	629.838 642.979 656.115 669.247 682.374	-10.813 -10.496 -10.385 -10.282 -10.184 -10.001
	3700 3800 3900 4000	82,875 82,889 82,903 82,915 82,926	470.701 479.032 481.243 483.396 485.496	402.902 404.988 406.965 408.898 410.786	203.070 273.964 282.254 290.545 298.837	223.109 223.158 223.190 223.207	708.622 721.745 734.865 747.984	- 10.091 10.004 9.921 9.842 9.768
	4100 4200 4300 4400 4500	82.946 82.956 82.956 82.964 82.972	487.343 489.542 491.494 493.401 495.266	412.034 414.441 416.210 417.943 419.641	307.130 315.424 323.719 332.015 340.312	223.209 223.199 223.178 223.145 223.104	761.104 774.223 787.343 800.463 813.584	-9.697 -9.629 -9.564 -9.503 -9.444
	4600 4700 4800 4900 5000	82.979 82.986 82.993 82.999 83.005	497.089 498.874 500.621 502.333 504.009	421.305 422.936 424.537 426.107 427.648	348,609 356,908 365,207 373,506 381,807	223.053 222.994 222.926 222.849 222.764	826.706 839.830 852.955 866.082 879.210	-9.388 -9.334 -9.282 -9.233 -9.185
	5100 5200 5300 5400 5500	83.010 83.015 83.020 83.025 83.029	505.653 507.265 508.846 510.398 511.922	429.162 430.648 432.109 433.544 434.955	390.107 398.409 406.710 415.013 423.315	222.670 222.565 222.451 222.324 222.185	892.340 905.471 918.606 931.741 944.879	-9.139 -9.096 -9.053 -9.013 -8.974
	5690 5790 5890 5990 6090	83,033 83,037 83,041 83,044 83,048	513.418 514.888 516.332 517.751 519.147	436.343 437.708 439.052 440.373 441.675	431.618 439.922 448.226 456.530 464.835	222.032 221.863 221.678 221.474 221.250	958.022 971.165 984.313 997.462 1010.617	- 8.936 - 8.900 - 8.865 - 8.831 - 8.798
	PREVIOU	S:				CL	JRRENT: Mar	<u>ch 1996 (1 bar)</u>

$M_r = 127.9022$ Bromine oxide (BrO₃)

 $\Delta H^{\circ}(298.15 \text{ K}) = [221 \pm 50] \text{ kJ} \cdot \text{mol}$

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MALCOLM W. CHASE

Bromine oxide (BrO₃)

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NIST-JANAF THERMOCHEMICAL TABLES FOR THE BROMINE OXIDES

Bromine Oxide (BrBrO)

Ideal Gas

M_r = 175.8074 Bromine oxide (BrBrO)

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MALCOLM W. CHASE

$(9/208 + 5/K) = (312.7 + 21.1 K^{-1} \cdot mol^{-1})$,	$\Delta_{\rm f} H^{\circ}(0 \text{ K}) = [183.7 \pm 20] \text{ kJ} \cdot \text{mol}^{-1}$ $\Delta_{\rm f} H^{\circ}(298.15 \text{ K}) = [168 \pm 20] \text{ kJ} \cdot \text{mol}^{-1}$	Enthalpy	Reference	Temperature	$r_{r} = \Gamma_{r} = 298.15$	ĸ	Standard Stat	e Pressure =	p° = 0.1 MPa
$5(296.15 \text{ K}) = [512.7 \pm 2] \text{ F K}$ (10)			-		<i>Т/</i> К	C;	S° -[($G^{\circ} - H^{\circ}(T_{\tau})]/T$	$H^{\circ}-H^{\circ}(T_{r})$	$\Delta_{\rm f} H^{\circ}$	$\Delta_{\rm f}G^{\circ}$	log Kr
	Electronic Lesstate	vel and Quantum Weight ϵ_r , cm ⁻¹ 0.0	<u>g</u> , [3]		0 50 100 150 200 250	.000) 35.814 . 42.429 46.014 48.247 49.997	.000 234,286 261,298 279,255 292,815 303,775	INFINITE 463.229 356.090 327.647 317.312 313.543	-13.138 -11.447 -9.479 -7.259 -4.899 -2.442	183.713 183.848 183.126 182.292 181.349 180.262	183.713 177.315 171.047 165.183 159.619 154.309	INFINITE - 185.239 - 89.346 - 57.522 - 41.688 - 32.241
	Vibrational Fre	equencies and Degeneracies ν , cm ⁻¹			298.15 300 400	51.385 51.433 53.530	312,704 313,022 328,128	312.704 312.705 314.750	.000 .095 5.351	168.000 167.928 137.218	150.730 150.623 151.179	-26.226 -19.742
		804 (1) [150] (1) 236 (1)			500 600 700 800	54.868 55.735 56.316 56.719 57.008	340.228 350.313 358.951 366.499 373 197	318.676 323.132 327.647 332.041 336.249	10.776 16.309 21.913 27.566 33.253	137.422 137.656 137.895 138.127	154.646 158.069 161.453 164.802 168.123	- 16.156 13.761 12.048 10.760 9.758
Point G Bond J Produc	Distances: Br-C Angle: Br-Br-C t of the Momert	= [1.69] Å; Br-Br = [2.51] Å = [113.1]° s of Inertia: $I_A I_B I_C$ = [13784.91	10 × 10	-11 ⁷] g ⁱ cm ⁶	1000 1100 1200 1200 1400 1500	57.222 57.384 57.509 57.608 57.687 57.752	379.215 384.677 389.676 394.283 398.555 402.537	340,250 344,044 347,642 351,054 354,297 357,381	38,965 44,696 50,441 56,197 61,962 67,734	138,554 138,554 138,925 139,089 139,238 139,371	171.420 174.698 177.958 181.204 184.438 187.662	8.954 8.296 7.746 7.281 6.881 6.535
Enthalpy of Formation For the four halogen oxide species, XXO(g determined the enthalpies of formation of ma isodesnic reaction energies. The calculated 298,15 K.	g) where $X = F$, C ary triatomic bror results suggested	I, Br, I, there is no experimenta nine compounds using a comb d that BrBrO is less stable that	al data re ination o an BrOB	lated to the enthalpy of formation. Lee ¹ f theoretical isomeric, homodesmic and r by 14.6 kcal·mol ⁻¹ (61.1 kJ·mol) at	1600 1700 1800 1900 2000	57.805 57.849 57.887 57.918 57.946	406,266 409,772 413,080 416,210 419,182	360.321 363.128 365.812 368.383 370.849	73.512 79.295 85.081 90.872 96.665	139.486 139.582 139.657 139.708 139.735	190.877 194.086 197.290 200.490 203.689	-6.231 -5.964 -5.725 -5.512 -5.320
Heat Capacity and Entropy Lee, ¹ using ab initio calculations – CCSD(Å, which we adopt. The principal moments The recommended vibrational frequencies	T) – derived a boo of inertia (in g or are those suggests	and angle of 113.1° and bond dis n°) are: $I_A = 4.7079 \times 10^{-39}$, I_A ed by Jacox. ² These results are	tances $r(B_{\rm B} = 51.80)$	Br-Br) = 2.510 Å and $r(Br-O) = 1.690$ 84 × 10 ⁻³⁹ , and $I_{\rm C} = 56.5163 × 10-39$. the infrared spectra of the argon matrix	2/00 2200 2500 2400 2500	57.969 57.989 58.007 58.023 58.037	422.010 424.707 427.285 429.754 432.123 434.400	373.219 375.498 377.694 379.812 381.858	102.461 108.259 114.059 119.860 125.663	139.734 139.704 139.643 139.550 139.426	206.886 210.085 213.285 216.488 219.697	-5.146 -4.988 -4.844 -4.712 -4.590
isolated radical as studied by Tevault <i>et al.</i> ³ initio calculations, derived the vibrational fre dations. Tevault <i>et al.</i> ⁴ observed very intense band pp light The assignments for BBPO were as	ι_2 is estimated by equencies to be 7 Is at 804 and 236 symmed to be v_1 =	ased on comparisons of the vib 93, 153 and 215 cm ⁻¹ . These rcm^{-1} which appeared when A = 804 cm ⁻¹ (Br–O stretch), v_1 =	orational are in ex Ar–Br ₂ –O = 236 cm	frequencies with CIOO. Lee, ' using ab cellent agreement with our recommen- matrices were photolyzed with 632.8 (Br-Br stretch) and the ν_2 value (the	2100 2100 2800 2900 3600	58.060 58.070 58.079 58.087 58.087	436.591 438.702 440.740 442.709	385.749 387.602 389.400 391.144 392.838	137.273 143.079 148.887 154.695	139.080 138.861 138.613 138.337	226.131 229.359 232.595 235.841 239.096	-4.375 -4.279 -4.189 -4.106 -4.029
References ¹ T. J. Lee, J. Phys. Chem. 99 , 15074–80 (19)	00 cm ⁻¹ .				3200 3300 3400 3500	58.101 58.107 58.112 58.117	446.459 448.246 449.981 451.666	394.485 396.088 397.647 399.167	166.314 172.124 177.935 183.747	137.714 137.372 137.013 136.640	242.361 245.636 248.922 252.219	-3.956 -3.888 -3.824 -3.764
² M. E. Jacox, J. Phys. Chem. Ref. Data, Mo ³ D. E. Tevault, N. Walker, R. R. Smardzewa	mograph No. 3, 4 sci, and W. B. 3	161 pp. (1994). ox, J. Phys. Chem. 82 , 2733 (1	1978).		3100 3100 3800 3900 4000	58.122 58.126 58.130 58.134 58.137	453.305 454.896 456.446 457.956 459.428	400.648 402.093 403.503 404.880 406.225	195.371 201.184 206.997 212.811	136.256 135.865 135.469 135.070 134.671	255.527 258.845 262.175 265.514 268.864	-3.708 -3.654 -3.604 -3.556 -3.511
					4 00 4200 4300 4400 4500	58.140 58.143 58.146 58.148 58.150	460.863 462.264 463.632 464.969 466.276	407.540 408.827 410.085 411.318 412.524	218.624 224.438 230.253 236.068 241.883	134.275 133.884 133.499 133.122 132.756	272.224 275.593 278.972 282.359 285.755	-3.468 -3.427 -3.389 -3.352 -3.317
					4600 4700 4800 4900 5000	58,153 58,155 58,157 58,158 58,160	467,554 468,805 470,029 471,228 472,403	413.707 414.866 416.002 417.117 418.211	247.698 253.513 259.329 265.144 270.960	132.400 132.056 131.726 131.409 131.106	289.158 292.570 295.989 299.415 302.846	-3.283 -3.252 -3.221 -3.192 -3.164
					5100 5200 5300 5400 5300	58.162 58.163 58.165 58.166 58.167	473.555 474.684 475.792 476.880 477.947	419.285 420.340 421.376 422.393 423.394	276.776 282.593 288.409 294.226 300.042	130.817 130.543 130.284 130.038 129.807	306.284 309.727 313.176 316.629 320.086	-3.137 -3.111 -3.087 -3.063 -3.040
					5500 5700 5800 5900 6000	58.168 58.170 58.171 58.172 58.173	478,995 480,025 481,036 482,031 483,008	424.377 425.345 426.296 427.232 428.154	305.859 311.676 317.493 323.310 329.127	129.589 129.384 129.192 129.012 128.842	323.548 327.013 330.482 333.954 337.429	-3.018 -2.997 -2.976 -2.957 -2.938
					PREVIOU	S:				CI	RRENT: Mar	ch 1996 (1 bar)

Bromine oxide (BrBrO)

7. Conclusions

Of the bromine oxides mentioned in the literature, only nine have been prepared (as a single crystal, or in the gas phase, or a matrix) and (at least, partially) characterized: BrO, BrBrO, BrOBr, OBrO, BrOO, Br_2O_3 , O_2BrBrO_2 , $O_2BrOBrO$, and Br_2O_5 . Only early studies exist which mention Br_2O_6 and Br_2O_7 ; it would appear that these species do not exist. BrO₃ and BrO₄ are proposed as intermediates in solutions or crystalline environments, with only an absorption maximum as a characterization.

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

In the following table, a summary of the recommended thermodynamic properties at ambient conditions for six bromine oxides are given. The brackets indicate estimated values. The recommended values contain significant uncertainties. In all cases, experimental enthalpy of formation data are needed. However, due to its importance in atmospheric chemistry, the prime effort should be directed at determining experimentally the enthalpy of formation of OBrO(g). Further efforts should be directed towards confirming the dissociation energy of BrO and the enthalpy of formation of BrO-Br(g), and establishing the enthalpies of formation for BrOO(g), BrBrO(g) and BrO₃(g). For any of the polyatomic gaseous species, except BrOBr, spectroscopic measurements for the geometry and vibrational frequencies would greatly reduce the uncertainties in the resulting thermal functions. Confirmation as to the existence of the various condensed phases is needed, although this is a much lower priority.

Heat capacity and enthalpy are not necessary at this time. (See Table 7.1.)

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

8. Acknowledgments

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9. References—Annotated Bibliographies

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

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