KINETIC STUDIES OF THE BROMINE–OXYGEN SYSTEM: A NEW PARAMAGNETIC PARTICLE, BrO₂

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The paramagnetic BrO₂ molecule with lifetime $\tau > 10$ s has been found among the products of the O + Br₂ reaction in a discharge flow system. Identification was made by the technique of molecular beam focusing in an inhomogeneous magnetic field with mass-spectrometric detection. Its symmetry appeared to be C_{2x}, like the stable OCIO molecule, as was determined by focusing in an inhomogeneous electric field. Approximate rate constants for the reactions O + BrO₂ ($k_5 \approx (2.5-6) \times 10^{-12}$ cm³/s) and Br + BrO₂ ($k_7 \approx 5 \times 10^{-11}$ cm³/s) were obtained.

1. Introduction

The BrO_x cycle is currently involved in speculations concerning processes which account for the destruction of the ozone layer in the earth's stratosphere in which Br and BrO are believed to be the active species of the cycle. This has given rise to marked interest in the chemical activity of BrO_x species.

The most suitable source of these particles in laboratory studies is the reaction

$$O + Br_2 \to BrO + Br \tag{1}$$

followed, in excess atomic oxygen, by the reaction

$$O + BrO \rightarrow Br + O_2.$$
 (2)

There have been several investigations of this system. In ref. [1], a discharge flow reactor has been used to determine the rate constant of reaction (1) and to estimate the rate constant of reaction (2) at 298 K. In a more recent investigation [2], Dodonov et al. made a comprehensive study of the mechanism of the reactions in the system containing O and Br atoms by mass-spectrometric probing of a diffusion cloud in a flow. Two kinds of BrO particles differing in their kinetic behaviour were recognized in that study and rate

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constants of reactions (1) and (2) for both of them have been obtained. Moin et al. [3] have measured a relative value of k_1 using ESR techniques.

In this work we have studied the secondary reactions and intermediate products in the $O + Br_2$ system by modulated-beam mass spectrometry assisted by beam analysis in inhomogeneous magnetic and electric fields. In particular, the presence of electronically excited states of the BrO radical has been tested by focusing in an electric lens. A new paramagnetic molecule BrO₂ with a lifetime greater than 10 s has been found and some of its molecular properties have been examined. Although we have failed to establish the origin of BrO₂, the approximate rate constants of its reactions with O and Br atoms have been determined.

2. Experimental

The molecular beam mass spectrometer for studying atomic and radical reactions has been described in detail elsewhere [4]. The experimental arrangement is shown in fig. 1. Pure O_2 (or Br_2), added to the carrier gas Ar or He and dissociating in a hf discharge (position 1) was used as a source of atomic oxygen (or bromine when needed). The $Br_2(2.5\%)$ -inert-gas mixture was admitted into a



Fig. 1. Scheme of the experimental arrangement. (1) Discharge; (2) reactor [reagent inlet through the capillary (c) or through the reactor (∞)]; (3) hexapole magnetic or electric lens; (4) chopper; (5) ion source; (6) magnetic mass analyser.

2.6 cm diameter reactor (position 2) through a glass capillary with a 0.28 mm inner and 0.78 outer diameter set at the reactor axis, providing a diffusive mixing of reactants. The Br₂ concentration in the diffusion cloud was $\approx 10^{13}$ cm⁻³. The absolute O-atom concentration in the reactor ranged from 10^{13} to 5×10^{14} cm⁻³ so that a pseudo-first-order dependence of the reaction on O-atom concentration was maintained in most experiments. The O-atom concentration was measured by chemiluminescent titration with NO₂ [5]. The reaction was studied at room temperature and at a total pressure of 4 Torr.

The molecular beam of the reaction mixture was formed in a nozzle-skimmer system with 0.4 mm diameter orifices separated by 4 mm, modulated at 33 Hz (position 4) and detected by a magnetic mass spectrometer (positions 5, 6). The sampling system provided a supersonic flow with Mach number M = 6, accompanied by translational and rotational cooling down to ≈ 30 K.

The distance x between the capillary tip and the sampling orifice could be varied from 4 to 13 mm. The flow velocity at the reactor axis was 10-16 m/s resulting in a typical contact time $\tau \approx 10^{-4}$ s.

To increase the relative sensitivity to atoms and free radicals, the molecular beam of reaction products was passed through a 15 cm long region of an inhomogeneous magnetic field of a hexapole focusing lens (position 3) before entering the ion source with 100 eV electron impact ionization (position 5). In the case of polar particles, the magnetic lens was substituted for an electrostatic hexapole one with 30 cm long poles. The technique of magnetic and electric beam focusing has been applied in a number of kinetic studies [6-8].

3. Results and discussion

Mass-spectral lines at m/e 79, 81, 95, 97, 111, 113, 158, 160, 162, 16 and 32 were present in mass spectra of the reaction mixture. The bulk of the lines at m/e 16 and 32 corresponded to atomic and molecular oxygen; lines m/e 158, 160 and 162 represent different isotopes of molecular bromine. The lines at m/e 111 and 113 (BrO₂⁺) could belong to either molecular lines of BrO₂ or fragmention lines from heavier Br- and O-containing parent molecules. The same situation applied in the case of the lines at m/e 95 and 97 (BrO⁺). For the identification of precursors of the lines at m/e 95 and 111, molecular-beam analysis in an inhomogeneous magnetic field was performed.

3.1. Analysis of reaction products by magnetic focusing

The increase in intensity of the signal being monitored at pertinent mass-spectral lines after switching on the magnetic field demonstrates the presence of paramagnetic atoms and free radicals in the beam. Furthermore, the position of the maximum of the focusing curve allows the mass of the focusing particle to be determined. The magnetic focusing curve (MFC) shows the dependence of the relative change in intensity of a given line $\Delta I/I_0$, where $\Delta I = I - I_0$, I and I_0 are the peak



Fig. 2. Magnetic focusing curves for Br (\Box), BrO₂ (Δ) and BrO+BrO₂ at [Br₂]/[Br₂]₀ = 0.88 (O) and 0.12 (•). Arrows indicate the calculated positions of the maxima for Br and BrO₂; solid line represents the calculated curve for the BrO radical.

heights with the magnetic field on and off respectively, on the magnetic field strength H_0 . The MFCs at m/e 79 (Br⁺), 95 and 111 are shown in fig. 2 (all the curves were reproducible at their isotopic lines m/e 81, 97 and 113). Arrows indicate the calculated positions of the maxima of the MFCs of Br and BrO₂. It was also verified that the MFC of bromine atoms produced in the reaction coincided with the control MFC of Br atoms produced by dissociation of Br2 in a discharge under the same sampling conditions. In the calculation of the BrO₂ maximum position, the mass value 111 and spin value 1/2 were used. It was concluded from the experimental MFCs that the magnetic effect at m/e 79 may be attributed to Br atoms and that at m/e 111 to BrO₂ radicals.

The MFCs at m/e 95 were obtained at different values of $\beta = [Br_2]/[Br_2]_0$, where $[Br_2]$ and $[Br_2]_0$ are the Br_2 concentrations near the sampling orifice with and without reaction respectively. Under pseudo-first-order conditions with $[O] \gg [Br_2]$ this value is related to the variable parameters by $\beta = \exp(-k_1 [O]\tau)$ and serves as a measure of the degree of Br_2 consumption in the reaction. In all experiments β was measured by the relative decrease of the intensity of the m/e 160 line after switching on the discharge generating O atoms. Closed circles correspond to $\beta = 0.12$ and open ones to $\beta = 0.88$. The solid line represents the calculated MFC for BrO in the ground ${}^{2}\Pi_{3/2}$ state.

It should be noted that unlike BrO_2 and other polyatomic radicals having a free spin, a strong spin-orbit coupling according to Hund's case "a" takes place in diatomic BrO [9], yielding a negligible total magnetic moment in the excited ${}^{2}\text{II}_{1/2}$ state (which is ≈ 0.1 eV above the ground ${}^{2}\text{II}_{3/2}$ state), so that only the ground state is paramagnetic. In the latter case the effective magnetic moment depends on the rotational state of the radical.

It may be seen from a comparison of the calculated MFC and that measured at $\beta = 0.88$ that at this β value the focusing effect is almost entirely due to BrO radicals. With increasing β the focusing effect increases with a pronounced growth at the maximum of the BrO₂ MFC. Hence, it was concluded that the MFC at m/e 95 is composed of molecular BrO and fragment BrO, signals. From the known MFC of BrO, and that of BrO at small β^{-1} , when BrO₂ focusing may be neglected, it was possible to estimate the BrO₂ contribution to the signal at m/e 95, which appeared to be \approx 9% at $\beta = 0.50$ and $\approx 20\%$ at $\beta = 0.12$. In addition, the approximate ratio 1:1 was obtained for the intensity of the m/e 95 and 111 lines in the mass spectrum of BrO₅.

Thus, BrO_2 and $BrO^{-2}\Pi_{3-2}$ radicals have been identified among the reaction products in magnetic focusing experiments.

3.2. Analysis of reaction products by electric focusing

Focusing of BrO₂ in an electric field was studied in order to determine its geometric structure. The electric focusing curve (EFC), i.e. the dependence of $\Delta I/I_0$ on the lens rode voltage, at m/e 111 is shown in fig. 3.

It is well known that in general, the shape of the EFC is determined by the constant value of the dipole moment μ_0 of a molecule, its symmetry and its rotational distribution which depends on rotational constants and temperature. In fig. 3 the EFC of BrO₂ is compared with that of the stable



Fig. 3. Electric focusing curve for $BrO_2(\Delta)$ compared with that for $CH_2Cl_2(O)$.

CH₂Cl₂ molecule. which is a slightly asymmetric top with $\mu_0 = 1.6$ D [10] and mass 84. Though a direct comparison of the EFCs for these particles is not straightforward, since the molecular characteristics of BrO₂ are unknown and may differ from that of CH₂Cl₂, the major factor determining the order of the Stark effect exhibited by the molecule is its symmetry. Fig. 4 shows two possible structures of BrO₂ – BrOO (C_s symmetry) and OBrO (C_{2v} symmetry). The bond length and bond angles proposed by Clyne and Cruse [11] for the four-centre intermediate complex Br–O–O–Br



Fig. 4. Molecular geometry of two possible BrO₂ structures: BrOO. $r_{Br-O} = 2 \text{ Å}$, $r_{O-O} = 1.5 \text{ Å}$, $\theta_{Br-O-O} = 120^{\circ}$ (at the left) and OBrO. $r_{O-O} = 2.9 \text{ Å}$, $\theta_{O-Br-O} = 118^{\circ}$ (at the right). The "b" axis is shown in the molecular c.m. coordinate system.

were taken for the C_s structure and analogy to the OClO molecule was adopted for C_{2v} structure. The calculated rotational constants are equal to A =1.86, B = 0.113, C = 0.107 cm⁻¹ for C, and A =1.02, B = 0.25, C = 0.20 cm⁻¹ for C_{2x}, showing that both structures are slightly asymmetric tops. In the case of C_{2x} symmetry, the dipole moment is directed along the "b" axis (molecular axis of the intermediate moment of inertia) and interacts with the electric field according to the second-order Stark effect as in the case of CH₂Cl₂. It is unlikely in the case of BrOO (which has no symmetry elements), that the dipole moment has no components along molecular axes other than "b", which would ensure stronger focusing at low voltage owing to the first-order Stark effect. As the EFCs of BrO₂ and CH₂Cl₂ are very similar (with rather close rotational constants), we concluded that BrO₂ has the symmetric OBrO structure similar to that of the OCIO molecule, and its dipole moment is approximately equal to that of CH₂Cl₂.

It has been deduced from kinetic measurements [2] that in reactions (1) and (2), BrO was produced and consumed as if it were present in two different states, denoted as BrO' and BrO''. Two sets of rate constants (k_1, k_2) for each state have been determined and the suggestion has been made that these states are the ${}^2\Pi_{3/2}$ and ${}^2\Pi_{1/2}$ electronic states. Using the data on electric focusing of BrO₂ and its contribution to the m/e 95 line, we were able to obtain the EFCs of BrO at different β in order to determine whether the excited BrO ${}^2\Pi_{1/2}$ radical was present in the reaction.

Unlike the magnetic case, where only the ground ${}^{2}\Pi_{3/2}$ state may be focused, both states are focusable in electric field. The ${}^{2}\Pi_{3/2}$ state is focused according to the first-order Stark effect due to the degeneration of levels with opposite directions of orbital momentum projection on the molecular axis. The ${}^{2}\Pi_{1/2}$ state is generally focused in accordance with the intermediate Stark effect. The solid curves in fig. 5 represent the calculated EFCs for ${}^{2}\Pi_{3/2}$ and ${}^{2}\Pi_{1/2}$ states performed for Hund's case "a" taking into account the rotational dependence of the effective dipole moment. A rotational constant B = 0.43 cm⁻¹ and dipole moment $\mu_0 = 1.55$ D from the ESR measurements [9,13] were used in the calculation. The intermediate Stark effect in



Fig. 5. Electric focusing curves for BrO at $[Br_2]/[Br_2]_0 = 0.82$ (O) and 0.19 (\bullet). Solid lines represent the calculated curves for the ${}^2\Pi_{3/2}$ and ${}^2\Pi_{1/2}$ states of BrO.

 ${}^{2}\Pi_{1/2}$ state was regarded as a first-order effect if the A-doubling constant, Δ , for a given rotational state was less than the interaction energy with the electric field, and as a second-order effect otherwise. Δ was obtained by the formula $\Delta = 4AB/\Delta E$, where A is the fine structure constant, ΔE the energy difference between the ground Π and the first Σ state, for which the dissociation energy was taken [10].

The open circles in fig. 5 represent the EFC obtained at $\beta = 0.82$, when the BrO₂ contribution is negligible: closed circles correspond to $\beta = 0.19$, and a correction for a BrO₂ contribution of 20%, as determined in the magnetic experiments above, was made when plotting this curve. Next fig. 6 shows the kinetic profiles of BrO' and BrO'' calculated according to the reaction mechanism proposed in ref. [2], giving approximate BrO' to BrO'' concentration ratios of 7:1 at $\beta = 0.82$ and 2:1 at $\beta = 0.19$. The difference in calculated EFCs for a mixture of ${}^{2}\Pi_{3/2}$ and ${}^{2}\Pi_{1/2}$ states in these proportions amounts to $\approx 25\%$ at high voltage. The experimental error is $\approx 3\%$ for the EFC at



Fig. 6. Calculated kinetic curves for BrO' and BrO' based on the reaction scheme of ref. [2]: $O + Br_2 \rightarrow BrO' + Br$, $k'_1 = 1.9 \times 10^{-11}$; $O + BrO' \rightarrow Br + O_2$, $k'_2 = 7.3 \times 10^{-11}$; $O + Br_2 \rightarrow BrO''$ + Br, $k''_1 = 2.5 \times 10^{-11}$; $O + BrO'' \rightarrow Br + O_2$, $k''_2 = 2.3 \times 10^{-11}$ (rate constants in cm³/s).

 $\beta = 0.82$ and $\leq 10^{\frac{1}{5}}$ for that at $\beta = 0.19$. The curves coincide within these error limits indicating that only one state has been detected. As the degree of observed focusing is more characteristic of a first-order Stark effect it may be concluded that this state is ${}^{2}\Pi_{3/2}$, the deviations between the experimental and calculated ${}^{2}\Pi_{3/2}$ curves being obviously due to the approximations made in calculations. Since in our experiments no electronically excited states of the BrO radical were apparent either in magnetic or in electric measurements, we suggest that BrO' and BrO'' are not different electronic states but one of them is a vibrationally excited state of the BrO ${}^{2}\Pi_{3/2}$ ground state.

3.3. Kinetic measurements

BrO and BrO₂ kinetic profiles are shown in fig. 7. The radical concentrations were measured as a function of $\ln([Br_2]_0/[Br_2])$, which under the con-



Fig. 7. (a) Concentrations of Br (\Box) and BrO (O) versus $\ln[[Br_2]_0/[Br_2]]$. \blacksquare is a point of absolute Br concentration measurement. The dashed line represents the calculated kinetic curve for BrO based on the reaction scheme (1) and (2). (b) BrO₂ concentration versus $\ln([Br_2]_0/[Br_2])$ measured by variation of $x(\nabla)$ and [O] (\triangle). Solid lines represent the calculated kinetic curves based on the reaction scheme (1). (2). (4) and (5).

ditions used is a linear measure of the product $[O]\tau$. The kinetic curves were obtained either by variation of [O], or by variation of τ through the displacement of the capillary. In the latter case the linearity of Br₂ intensity with the inverse distance x was tested in each run and the measured signal was normalized according to the change in $[Br_2]$.

The height of the m/e 95 peak in the presence of an electric focusing field was taken as a measu, e of the BrO concentration at an intermediate voltage 6 kV at which the contribution of BrO₂ to the focused signal is small.

Br and BrO₂ concentrations were assumed to be proportional to the paramagnetic signal ΔI at m/e79 and m/e 111 respectively, measured at magnetic field strengths 2 and 4 kOe where maxima of their MFCs occur. The kinetic profiles of BrO₂ were determined by variation of both x and [O]. The kinetic curve for BrO obtained at x = const confirms its rapid consumption in reaction (2). Comparison with the calculated kinetic curve taking into account only reactions (1) and (2) with $k_1 = 1.4 \times 10^{-11} \text{ cm}^3/\text{s}$ and $k_2 = 3 \times 10^{-11} \text{ cm}^3/\text{s}$ [1] (dashed line in fig. 7a) shows that the experimental fall of the BrO concentration is somewhat slower than that predicted by this calculation.

The kinetic curve for BrO_2 shows that it is formed and, in turn, consumed in secondary reactions. The only important secondary reactions were those of intermediate products with O and O₂, since the quasistationary concentrations of intermediates were too small.

One of the possible channels of BrO₂ formation

$$Br + O_2 + M \to BrO_2 + M \tag{3}$$

was tested in a direct manner. For this purpose a known flow ($\approx 7 \times 10^{18} \text{ s}^{-1}$) of molecular oxygen was admitted through the capillary while a Br₂ (11%)-Ar mixture was passed through the discharge tube, providing a Br concentration of $\approx 10^{14}$ cm⁻³ in the reactor. The paramagnetic signal at m/e 79 was monitored under these flow conditions. No change in the Br concentration was observed within the error limits of 10%. According to ref. [4] this means that the bimolecular rate constant k_3 of reaction (3) is less than 1×10^{-12} cm³/s ($k_{\text{trimolecular}} < 5 \times 10^{-30}$ cm⁶/s) and, hence, reaction (3) is not important.

Another possible channel

$$O + BrO + M \rightarrow BrO_2 + M$$
 (4)

was tested by computer modelling of the reaction scheme (1), (2), (4) with the reaction

$$O + BrO_2 \rightarrow BrO + O_2 \tag{5}$$

taken as the most likely decay path for BrO₂. The calculated kinetic profiles are shown in fig. 7 by solid lines and corresponds to $k_4 = 5 \times 10^{-11}$ cm³/s and $k_5 = 2.5 \times 10^{-11}$ cm³/s obtained by least-squares fitting. Experimental intensities were normalized to calculated concentrations by the least-squares procedure after each iteration. These k_4 and k_5 values are the best to satisfy the Br, BrO and BrO₂ kinetic profiles simultaneously. As may be seen from fig. 7b this model yields rather poor

agreement with experiment.

We performed a direct test of this channel in the absence of Br_2 . For this purpose BrCl was synthesized by mixing Cl₂ and Br_2 as in ref. [1]. In that work the reaction O + BrCl was found to produce BrO:

$$O + BrC! \rightarrow BrO + Cl, \tag{6}$$

with rate constant $k_6 = 2.2 \times 10^{-11}$ cm³/s which is rather close to k_1 . Typical BrCl concentrations used in our experiments were of the order 2×10^{13} cm⁻³, the O-atom concentration was 10^{14} cm⁻³, so that the amount of BrO produced was the same as in the O + Br₂ system. Under these conditions no BrO₂ was found.

3.4. Influence of surface processes

Thus, the kinetic behaviour of BrO_2 cannot be described on the basis of being formed purely by gas-phase processes. At the same time, the dependence of $[BrO_2]/[Br_2]$ on both [O] and x, which passes through a maximum (fig. 8), shows that a simple model of heterogeneous formation of BrO_2 on the surface of the sampling cone is unacceptable. If we assume that the wall process depends linearly on the Br_2 concentration and obeys a square law on the concentration of O atoms, a square $[BrO_2]/[Br_2]$ dependence should be observed. Another possible wall process $BrO + O \xrightarrow{wall}$



Fig. 8. BrO₂ to Br₂ concentration ratio versus $\ln([Br_2]_0/[Br_2])$ measured by variation of $x (\bullet, \bullet)$ and [O] (O).

 BrO_2 is described by the product [BrO] [O] which is an increasing function of the O concentration without falling parts as may be seen from the kinetic dependence of BrO in fig. 7a, where the abscissa is linearly related to [O].

Another possibility is BrO₂ formation on the outer surface of the capillary. In this case the capillary surface may be considered as a BrO₂ source of constant strength. Then, according to the diffusion cloud formalism discussed in ref. [4], the $[BrO_{2}]/[Br_{2}]_{0}$ ratio would remain constant when x changes if BrO₂ does not react with O atoms and would exponentially decrease when x increases if this reaction occurs. In any case there is no agreement with experimental data. It should be emphasized that the method of a diffusion cloud in a flow is applicable if the diffusion takes place from a point source, which is regarded to be the capillary tip. In the present situation molecular bromine may spread over a great part of the capillary surface, creating an extended source which complicates the interpretation of the data.

To test the influence of the surface, the sampling cone made of stainless steel was covered with a Teflon suspension and sintered at 370°C for 15 min with further bake-out at 140°C for 30 min. The outer surface of the capillary and the inner surface of the reactor tube were subjected to the same treatment. After the surface treatment, BrO_2 was found only in O + Br₂ reaction as before. The BrO₂ formation is likely to require the presence of active centres occupied by Br₂.

3.5. Experiments in a flow reactor with complete mixing

Some experiments concerning BrO_2 were performed with Br_2 sampling at the bottom of the reactor tube (" ∞ " in fig. 1) as in conventional flow reactors. The mean reaction contact time in these experiments was $\approx 10^{-1}$ s. There was no paramagnetic signal at m/e 111 in the course of the reaction when Ar was used as a carrier gas, but as soon as the reaction had been stopped by switching off the discharge (i.e. removing O atoms) a signal was observed over an extended time interval. A typical time profile is shown in fig. 9 where the arrow indicates the moment of switching off



Fig. 9. m/e 111 signal in O + Br₂ system under the condition of complete mixing of the flow. Arrow indicates switching off the discharge. Time constant of the recording system is 6 s.

the discharge. The same "post-effect" was observed for the isotopic line at m/e 113; there was no effect at molecular lines of BrO₃ (m/e 127). BrO_4 (m/e 143) and Br_2O_2 (m/e 192) confirming that the effect at m/e 111 could not be attributed to these species. The peak ion current of this signal was of the same order of magnitude as the Br₂ steady ion current without reaction. Taking into account the equal line intensity at m/e 95 and m/e 111 in the mass spectrum of BrO₂ and assuming the same instrumental sensitivity to Br₂ and BrO₂, the number of BrO₂ particles detected in the post-effect pulse was estimated to $\approx 10^{17}$. A signal of such duration leads to the conclusion that the post-effect is due to the BrO2 particles which left the reactor wall in the absence of O atoms (after the reaction had stopped). BrO₂ leaving the reactor wall in the course of the reaction react with O atoms and thus do not reach the detector. This conclusion was supported by experiments with He carrier gas, in which the BrO2 signal was observed during the reaction as well as afterwards.

Furthermore, it was found that the post-effect signal intensity depended on the duration of the preceding reaction: the longer the discharge had been on, the greater the peak intensity. This indicates that BrO_2 had been accumulating on the wall

of the reactor in the course of the reaction. It may be seen that at rather large O concentration $(5 \times 10^{14} \text{ cm}^{-3})$ the stationary surface concentration of BrO₂ is attained in ≈ 4 min (see fig. 10), while at an O concentration of $1 \times 10^{14} \text{ cm}^{-3}$, even a 10 min period appears to be too short to obtain saturation.

Let us estimate the time for BrO_2 to diffuse from the reactor wall to the axis. The diffusion coefficients of BrO_2 in Ar and He, $D_{\text{BrO}_2-\text{Ar}} = 22.2$ cm^2/s and $D_{\text{BrO}_2-\text{He}} = 97.6$ cm^2/s were calculated using Fuller's expression [14], which gives for the diffusion time in Ar and He $\tau_{\text{Ar}} \approx R^2/2D_{\text{BrO}_2-\text{Ar}}$ $= 2 \times 10^{-2}$ s and $\tau_{\text{He}} \approx R^2/D_{\text{BrO}_2-\text{He}} = 4 \times 10^{-3}$ s. *R* denoting the reactor tube radius. Hence, only molecules desorbing at a distance larger than 8 cm in Ar and 1.5 cm in He from the sampling orifice could by detected. As the diffusion time in He is considerably smaller than that in Ar. reaction (5)



Fig. 10. Dependence of BrO_2 ion current (in terms of peak intensities in fig. 9) on the duration of the preceding reaction at $[O] = 1 \times 10^{14} \text{ cm}^{-3}$ (upper part) and at $[O] = 5 \times 10^{14} \text{ cm}^{-3}$ (lower part).

is not sufficient to remove BrO_2 which results in the "direct" effect, i.e. the paramagnetic signal at m/e 111 during the reaction carried out in He.

The lower limit for the rate constant of reaction (5) may be obtained: $k_5 > 1/[O]_{Ar}$ $\tau_{Ar} = 0.5 \times$ 10^{-12} cm³/s, where [O]_{Ar} is the minimal O concentration used in the experiments with Ar under the condition $[O] \gg [Br_2]$. The O concentration in these experiments was determined from the Br₂ consumption in a diffusion cloud and the known k_1 and equalled 1×10^{14} cm⁻³. Under the condition $[Br_2]_0 \gg [O]$ in Ar, where O atoms were expected to be removed by the reaction shortly after mixing, the direct effect was again not observed. This may be explained by the fast reaction of BrO_{2} with Br atoms generated in the reaction $O + Br_2$. The Br-atom concentration was assumed to be equal to the initial O concentration ($\approx 10^{12} \text{ cm}^{-3}$). giving as the lower limit for the rate constant of the reaction

 $Br + OBrO \rightarrow BrO + BrO$ or $Br_2 + O_2$ (7)

the value $k_7 > 1/[Br]_{Ar}\tau_{Ar} = 5 \times 10^{-11} \text{ cm}^3/\text{s}.$

The direct effect in He was examined with $[O] \gg [Br_2]$ at different O concentrations. The results are listed in table 1.

From these data an upper limit for k_5 may be obtained using the maximal O concentration for which the effect is still observed ([O]_{max} = 4.3 × 10^{13} cm⁻³), $k_5 < 1/[O]_{max} \tau_{He} = 6 \times 10^{-12}$ cm³/s. The next [O] value, 10^{14} cm⁻³, at which the BrO₂ signal practically disappears, gives a lower limit $k_5 > 1/[O] \tau_{He} = 2.5 \times 10^{-12}$ cm³/s. As the latter inequality is stronger than the above, we have for k_5 a range of $(2.5-6) \times 10^{-12}$ cm³/s. One may

Table 1 BrO₂ (m/e 111) paramagnetic signal during the reaction O+ Br₂ in He. [Br₂]₀ = 8×10^{12} cm⁻³

[O] (10 ⁻¹⁴ cm ⁻³)	کی (arb. units)	
0.08	0	
0.12	5±2	
0.20	5 <u>+</u> 1	
0.24	25 ± 2	
0.43	18 ± 3	
1.0	0	

assume that under these conditions a considerable amount of Br₂ is converted into Br so that [Br] \approx [Br₂]₀. The presence of detectable amounts of BrO₂ permits us to estimate $k_7 < 1/[Br] \tau_{He} = 3 \times 10^{-11} \text{ cm}^3/\text{s}$, which is of the same order of magnitude as that estimated above.

These rough estimates of the rate constants k_5 and k_7 may be compared with the rate constants for the analogous chlorine reactions:

$$O + ClO_{2} \rightarrow ClO + O_{2} \tag{8}$$

and

$$Cl + ClO_2 \rightarrow ClO + ClO.$$
 (9)

with $k_8 = 5 \times 10^{-13}$ cm³/s [15] and $k_9 = 5.9 \times 10^{-11}$ cm³/s [16]. Our evaluation of the rate constant for the Br + BrO₂ reaction is close to that of reaction (9), so it is very likely that the channel forming two BrO radicals proceeds in this case also. The estimated rate constant for the O + BrO₂ reaction appeared to be somewhat faster than k_8 .

Neither the peroxide (BrOO) nor the symmetric (OBrO) form of BrO_2 has been detected in the gas phase, though Sander and Watson in their work on the mechanism of the disproportionation reaction BrO + BrO [17] have postulated the existence of BrOO radicals as an intermediate species:

$$BrO + BrO \rightarrow BrOO + Br.$$
 (10)

$$BrOO + M \to Br + O_2 + M. \tag{11}$$

A different version of the mechanism suggested the formation of the excited $Br_2O_2^*$ complex:

$$BrO + BrO \rightarrow Br_2O_2^* - \underbrace{M}_{BrOO}^{M} Br_2O_2 \qquad (12)$$

In either case the fast reaction (11) was assumed to result in a rapid decay of BrO_2 which prevented the detection of this particle. From this, the authors evaluated the Br–OO bond energy as 1 kcal/mol.

On passing a gaseous mixture of Br_2 and O_2 through a dc discharge cooled by fluid air. Schwarz and Schmeisser [18] observed the formation of a solid substance that decomposed at 0°C. The obtained ratio of molecular bromine to oxygen quantities produced by this decomposition enabled them to determine this substance as being BrO_2 .

The results given above confirm that BrOO

cannot exist in the gas phase and suggest the formation of $Br_n O_{2n}$ in the solid phase.

4. Conclusion

 BrO_2 were identified in a flow reactor system containing molecular and atomic bromine and oxygen. Its geometry was determined as OBrO, resembling the stable OCIO molecule. Its ability to accumulate on the surface and further to be detected at room temperature confirm that it is a stable paramagnetic molecule.

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