J. Chem. Soc., Faraday Trans. 2, 1982, **78**, 1383–1389

Rate Coefficient for the Reaction of BrO with HO_2 at 303 K

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Received 29th January, 1982

The kinetics of the reaction of BrO with HO_2 have been investigated using the photolysis of O_3 in the presence of Br_2, H_2 and O_2 as a source of these radicals. The molecular-modulation–u.v.-absorption technique was employed to observe directly the behaviour of both BrO and HO_2 in the modulated photolysis system and to obtain a value for the rate coefficient for the reaction

$$BrO+HO_2 \rightarrow HOBr+O_2 \qquad (3a)$$

$$\rightarrow HBr+O_3 \qquad (3b)$$

at 303 K. The value obtained was $k_3 = 5^{+5}_{-3}\times 10^{-12}$ cm^3 molecule^{-1} s^{-1}

The reactions of BrO are currently of interest from the point of view of atmospheric chemistry, since on the basis of early work of Clyne and Cruse[1] it has been hypothesised[2] that Br and BrO can act as catalysts for the destruction of ozone in the stratosphere through reactions such as

$$Br+O_3 \rightarrow BrO+O_2 \qquad (1)$$

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

Watson *et al.*[3] have shown that the catalytic efficiency of BrO_x in O_3 destruction is a strong function of the fraction of total BrO_x which is in the active form BrO (and Br). Reactions that convert Br and BrO into other more stable bromine-containing species, *e.g.* HBr, HOBr and $BrONO_2$ (bromine nitrate), are therefore important in determining the efficiency of O_3 destruction by these species. The reaction of BrO with HO_2

$$BrO+HO_2 \rightarrow HOBr+O_2 \qquad (3a)$$

$$\rightarrow HBr+O_3 \qquad (3b)$$

has been suggested[3] by analogy with the similar reaction of ClO, which is now reasonably well characterised.[4,5] However, there appears to be no experimental evidence for the occurrence of reaction (3) or any measurements of its rate coefficient.

In this paper we report a study designed to provide information on reaction (3). The technique of photochemical modulation spectrometry has been employed to observe directly the behaviour of BrO and HO_2 in the 254 nm photolysis of $O_3+Br_2+H_2+O_2$ mixtures, diluted in N_2 at 1 atm pressure.† Ozone photolysis in the presence of Br_2, O_2 and N_2 leads the production of BrO *via* the reactions

$$O_3+h\nu \rightarrow O(^1D)+O_2(^1\Delta) \qquad (4)$$

$$O(^1D)+N_2 \rightarrow O(^3P)+N_2 \tag{5}$$

$$O_2(^1\Delta)+O_3 \rightarrow O(^3P)+2O_2 \tag{6}$$

$$O(^3P)+Br_2 \rightarrow BrO+Br \tag{7}$$

$$O(^3P)+O_2+N_2 \rightarrow O_3+N_2. \tag{8}$$

BrO is removed in the bimolecular disproportionation reactions

$$BrO+BrO \rightarrow 2Br+O_2 \tag{9}$$

$$BrO+BrO \rightarrow Br_2+O_2 \tag{10}$$

as was shown in our previous work on this system.[6] However, the "radical" channel reaction (9) yielding $2Br+O_2$ does not lead to net removal of BrO because of its fast regeneration by reaction (1)

$$O(^1D)+H_2=OH+H. \tag{11}$$

When H_2 is present reaction (11) occurs in competition with reaction (5) leading to the production of HO_2 *via* the reactions

$$H+O_2+M \rightarrow HO_2+M \tag{12}$$

$$OH+O_3 \rightarrow HO_2+O_2. \tag{13}$$

When the concentrations of H_2 and Br_2 are such that BrO and HO_2 are produced photochemically at similar rates the interaction of HO_2 with BrO can then be investigated in competition with their respective mutual reactions, *i.e.* reaction (10) and

$$HO_2+HO_2 \rightarrow H_2O_2+O_2. \tag{14}$$

In view of the large number of side reactions occurring in the photochemical system, detailed analysis of the kinetic data to obtain values for the rate coefficients for reactions (3), (10) and (14) was conducted in this work using numerical simulation techniques.

EXPERIMENTAL

Gaseous mixtures of $O_3+Br_2+H_2+O_2$ diluted in N_2 at 1 atm pressure flowed through the 86 cm × 2 cm jacketed silica reaction cell which was illuminated by square-wave modulated 254 nm light from a 40 W low-pressure Hg lamp (Philips TUV 40). Absorption was monitored in the long axis of the cell on a beam from a D_2 lamp which was dispersed on a Spex Doublemate monochromator and detected on a photomultiplier. BrO was monitored at 338.3 nm, the band head of the 7–0 band of the $A\,^2\Pi \leftarrow X\,^2\Pi$ transition, with a spectral slit width of 0.6 nm. The absorption cross-section for BrO at this resolution was determined relative to that at high resolution[6] in separate experiments. The value obtained was 1.5×10^{-17} cm^2 molecule^{-1}. HO_2 was monitored at 210 nm ($\sigma = 4.3\times10^{-18}$ cm^2 molecule^{-1}) and correction for absorption due to O_3 at this wavelength was applied in the manner described elsewhere.[7,8]

In the present work two methods were employed for detection of the absorption signals due to the photochemically modulated transient species. For rapid monitoring of BrO behaviour as a function of changing mixture composition, the previously described digital lock-in system was used to obtain in-phase and in-quadrature components of modulated absorption.[7,9] For observation of the time-resolved waveform of absorption during a photolysis period, the multichannel analyser system, which is described in detail in ref. (6), was used. This method was used to monitor the time–concentration behaviour of both BrO and HO_2 during the photolysis cycle. Experiments were all conducted at 303 K.

RESULTS

The photolysis of $O_3 + Br_2 + O_2$ mixtures in the absence of added H_2 gives rise to strong modulated absorption due to BrO at 338 nm. In this system BrO exhibited second-order behaviour with an overall decay rate coefficient attributed to reaction (10) of $(6.0 \mp 1.3) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} obtained by simulation of the BrO absorption profile.

Mixtures containing O_3, O_2 and H_2 but no Br_2 exhibited absorption in the u.v. near 210 nm attributable to HO_2. HO_2 also exhibited second-order kinetic behaviour with a rate coefficient $k_{14} = (2.5 \mp 0.3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. These measurements, obtained by simulation of the HO_2 profile in 3 experiments using different photochemical production rates were also used to determine k_4, the photodissociation coefficient for O_3, in the manner described before.[7] The value obtained was 2.2×10^{-2} s^{-1} for photolysis using a single 40 W lamp. The values of k_4, k_{10} and k_{14} agree well with previous determinations in our apparatus.[6,7]

The effect of added H_2 on BrO was investigated by observation of the in-phase (P) and in-quadrature (Q) absorption components at 338.3 nm. Fig. 1(a) shows

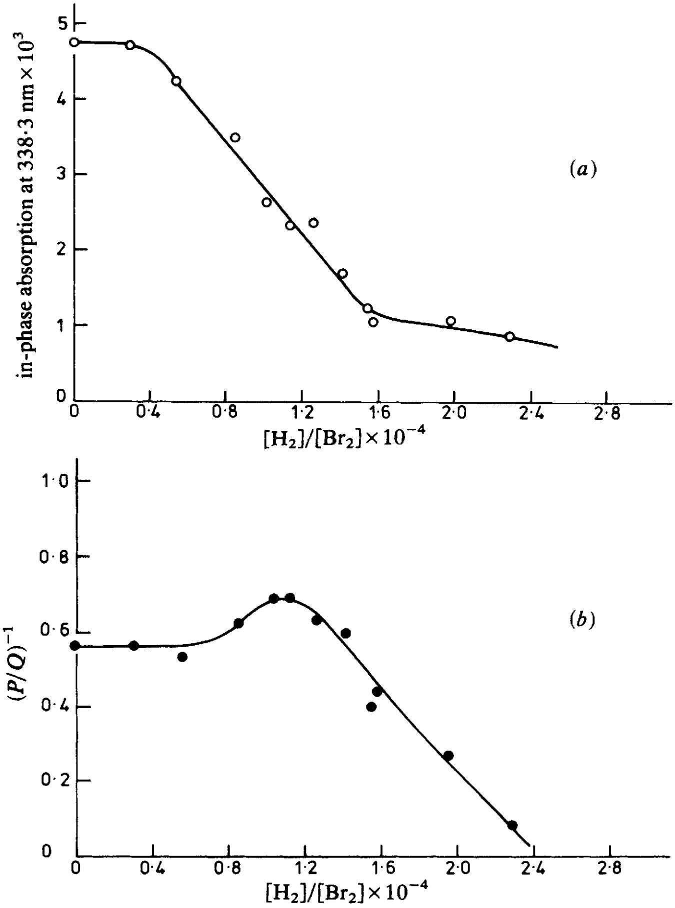

FIG. 1.—Effect of varying the ratio $[H_2]/[Br_2]$ on (a) the in-phase absorption due to BrO at 338.3 nm and (b) the ratio $(P/Q)^{-1}$ (P = in-phase, Q = in-quadrature absorption) in the 254 nm photolysis of $O_3 + Br_2 + H_2 + O_2 + N_2$ mixtures at 1 atm pressure.

the effect of increasing the ratio $[H_2]/[Br_2]$ on the concentration modulation of BrO, as measured by the in-phase absorption component. The average concentrations of Br_2, O_2 and O_3 in these experiments were *ca.* 1.0×10^{14}, 1.3×10^{18} and 1.0×10^{15} molecule cm^{-3}, respectively. It will be seen that BrO absorption decreased steadily as the ratio $[H_2]/[Br_2]$ increased. The relative photochemical production rates of HO_2 and BrO are determined by the competition between reactions (11) and (5) followed by a further competition for $O(^3P)$ between reactions (7) and (8). For the concentrations of O_2, O_3 and N_2 used in these experiments the production rates of BrO and HO_2 were approximately equal at $[H_2]/[Br_2] = 1\times10^4$, and at this ratio BrO absorption was reduced by a factor of 2 from that when $[H_2] = 0$. Fig. 1(*b*) shows the ratio $(P/Q)^{-1}$ plotted against $[H_2]/[Br_2]$. The quantity Q/P is a measure of the phase-shift of the modulated absorption relative to the photolytic light source and reflects the lifetime of the transient species. It will be seen that initially the lifetime of BrO tended to increase as BrO concentration decreased with increasing H_2. This is the expected behaviour if BrO removal is dominated by the second-order decay reaction (10). However, when sufficient H_2 has been added to produce HO_2 at a rate approximately equal to the rate of BrO production (*i.e.* $[H_2]/[Br_2]\approx 1\times10^4$), the lifetime of BrO decreased rapidly, whilst at the same time [BrO], as reflected in the magnitude of the in-phase absorption, continued to decrease. This behaviour is consistent with the occurrence of a fast reaction between HO_2 and BrO, which dominates the decay of BrO when sufficient HO_2 is present.

In order to determine the rate coefficient for the reaction of BrO with HO_2, the full concentration–time behaviour of both radicals was measured in duplicate experiments under the same conditions, but monitoring at different wavelengths. Experimental results were obtained using different mixture compositions corresponding to excess BrO production, excess HO_2 production and approximately equal production of BrO and HO_2. Fig. 2 shows full concentration–time curves for HO_2 and BrO in 0.5 Hz photolysis of an $O_3+Br_2+H_2+O_2$ mixture with excess HO_2

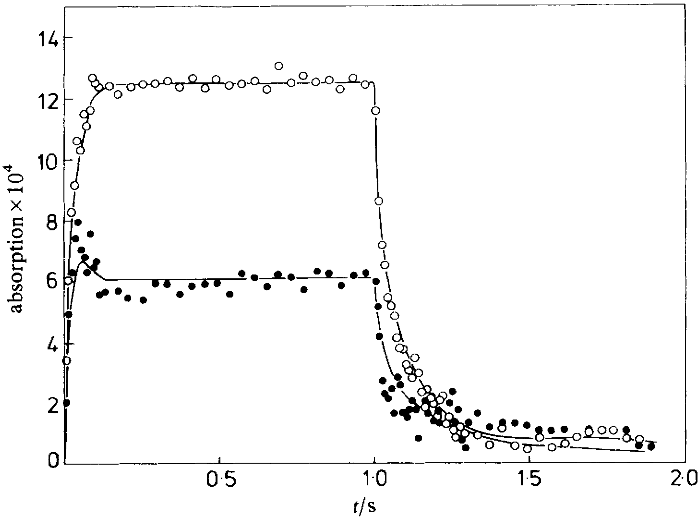

FIG. 2.—Absorption-time profiles for HO_2 (○, 210 nm) and BrO (●, 338.3 nm) in the 0.5 Hz photolysis at 254 nm of an $O_3+Br_2+H_2+O_2+N_2$ mixture; total pressure = 1 atm, averaging time = 1200 s, steady-state concentrations of HO_2 and BrO are 3.4×10^{12} and 4.8×10^{11} cm^{-3}, respectively.

production. It will be seen that on photolysis both radicals rise rapidly and attain a steady state after *ca.* 100 ms. When photolysis ceases, BrO falls rapidly in the first 10–20 ms and then rather slowly during the remainder of the dark period; HO_2 decays with a first half-life of *ca.* 40 ms. If BrO were only removed by reaction (10) the time to decay to 50% of the steady-state absorption would be 1.8 s; clearly there is an additional rapid process removing BrO, the initial decay rate being *ca.* $20\ s^{-1}$. Since $[HO_2]$ is initially 3.4×10^{12} molecule cm^{-3}, based on the steady-state absorption, one may estimate a value of $6\times10^{-12}\ cm^3$ molecule^{-1} s^{-1} for k_3.

A value for k_3 may also be estimated from the steady-state absorptions of HO_2 and BrO. Assuming that the radicals are removed only by reactions (3), (10) and (14), the following rate equations can be derived

$$\frac{d[HO_2]}{dt}=B_{HO_2}-k_3[BrO][HO_2]-2k_{14}[HO_2]^2 \tag{i}$$

$$\frac{d[BrO]}{dt}=B_{BrO}-k_3[BrO][HO_2]-2k_{10}[BrO]^2 \tag{ii}$$

where B_{HO_2} and B_{BrO} are the photolytic production rates of HO_2 and BrO, respectively. The steady-state solutions of eqn (i) and (ii) are, respectively,

$$-k_3[BrO]_s=2k_{14}[HO_2]_s-\frac{B_{HO_2}}{[HO_2]_s} \tag{iii}$$

$$-k_3[HO_2]_s=2k_{10}[BrO]_s-\frac{B_{BrO}}{[BrO]_s} \tag{iv}$$

where $[\ ]_s$ refers to the steady-state concentrations of BrO and HO_2. For the conditions of the experiment shown in fig. 2, B_{HO_2} and B_{BrO} were 6.7×10^{13} and 9.5×10^{12} molecules $cm^{-3}\ s^{-1}$, respectively, these values being calculated using the measured average concentrations of O_3 and Br_2 present in the cell and rate coefficients for the various elementary reactions of Br, BrO, $O(^1D)$, $O(^3P)$ and $O_2(^1\Delta)$ from recent evaluations.[10,11] Using $k_{10}=6.0\times10^{-13}\ cm^3$ molecule^{-1} s^{-1} and $k_{14}=2.5\times10^{-12}\ cm^3$ molecule^{-1} s^{-1} gives values of $k_3=6.4\times10^{-12}$ and $k_3=5.8\times10^{-12}\ cm^3$ molecule^{-1} s^{-1} from eqn (iii) and (iv), respectively.

In view of the potential uncertainties arising from simple steady-state analysis and the role of minor side reactions, full computer simulation of the BrO and HO_2 concentration–time behaviour was conducted using FACSIMILE.[12] In addition to reactions (1)–(14), reactions of OH with H_2 and HO_2, reaction of HO_2 with O_3 and $O(^3P)$ and quenching reactions of $O(^1D)$ and $O_2(^1\Delta)$ by O_2 were included in the chemical scheme. Rate coefficients were preferred values from ref. (10) and (11), except for k_{10} and k_{14} for which the values obtained in this study were used. The value of k_3 was varied to obtain an optimised fit to each experimental data set, comprising both HO_2 and BrO absorption profiles. The criterion for the best fit was minimum sum of squares of differences between the calculated and observed absorptions for 20 time points during a photolysis cycle, each weighted by the estimated experimental uncertainty of 1×10^{-4} absorption units. The value of k_3 was systematically adjusted in the routine and the optimisation was considered to have converged when the residual sum of squares no longer decreased. The results for different BrO and HO_2 production rates are shown in table 1, where the 5–95% confidence limits were derived from the sensitivity of the residuals to the value of

TABLE 1.—BEST-FIT VALUES OF k_3 FROM COMPUTER SIMULATION OF BrO AND HO_2 ABSORPTION PROFILES

$[Br_2]/10^{13}$ molecule cm^{-3}	$[H_2]/10^{18}$ molecule cm^{-3}	B_{HO_2}/B_{BrO}	$k_3/10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}
9.6	19.4	7.0	4.0 ± 0.4^a
11.0	1.64	1.47	4.3 ± 0.3
39.0	2.00	0.61	2.3 ± 0.2

[a] Data from fig. 2; the corresponding computed curves are shown in fig. 2.

k_3 and do not reflect systematic errors from experimental sources or model assumptions. The experiments with excess HO_2 both gave values close to 4×10^{-12} cm^3 $molecule^{-1}$ s^{-1} but a lower value was obtained when BrO production dominated. This reflects possible systematic error which is much larger than the statistical error given by the fitting process indicated in the table. It was also found that the value of k_3 obtained from the fit was very sensitive to the Br_2 concentration which was treated as a fixed parameter in the simulation. Since up to 70% of the initial Br_2 reacted during passage through the reaction cell, only an average value of $[Br_2]$ could be used and this could be a source of error in the fitted values and those obtained from eqn (iii) and (iv). The higher values obtained from steady-state analysis reflect the neglect of reactions other than reactions (3), (10) and (14) which remove radicals. Furthermore, since $[HO_2]$ and [BrO] have non-zero values at the end of the photolysis cycle, the steady-state concentrations will tend to be underestimated from the absorption–time profiles, also leading to overestimation of k_3. The overall error is estimated to be ± *ca.* 2. The best estimate based on the simulations and the steady-state analysis is

$$k_3 = 5^{+5}_{-3} \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 303 K}$$

DISCUSSION

Although the determination of k_3 from this study is not very precise, it is clear from the results that a moderately rapid reaction occurs between HO_2 and BrO at room temperature. There appear to have been no previous experimental determinations of this rate coefficient although recent evaluations[10] have suggested a value of $k_3 = 5 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} for use in atmospheric modelling. This is based on analogy with the reaction of ClO with HO_2 which has been fairly extensively studied over a wide range of pressure and temperature and has a room-temperature value of 6×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. The present results are therefore consistent with the general pattern of reactivity exhibited by halogen oxide radicals with HO_2, O, NO and NO_2.

The present work does not provide identification of the products of reaction (3) but the observations require that the products do not react rapidly in the system to yield BrO and/or HO_2 on the timescale of the measurements. Channels yielding $HOBr + O_2$ or $HBr + O_3$ would both be consistent with this requirement. It is probable, again by analogy with the reaction of ClO with HO_2, that HOBr formation is the major channel.

This work was performed as part of an Atmospheric Chemistry project funded jointly the U.K. Department of Environment and the E.E.C. Environment Programme under contract no. ENV-454-UK.

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