EPR DETERMINATION OF ABSOLUTE RATE CONSTANTS FOR THE REACTIONS OF H AND OH RADICALS WITH HYDROGEN BROMIDE

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The absolute rate constants for the reactions of H atoms and OH radicals with HBr were measured by the discharge flow technique with EPR detection. The rate constants at room temperature are $k_1 = (6.3 \pm 0.5) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ for H + HBr \rightarrow H₂ + Br and $k_2 = (9.2 \pm 0.7) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ for OH + HBr \rightarrow H₂O + Br. There is a discrepancy between measurements carried out by the EPR-discharge flow and flash photolysis-resonance fluorescence techniques.

1. Introduction

Hydrogen bromide is known to be an efficient inhibitor of flame propagation (e.g. refs. [1-3]). It is generally agreed that inhibition results from reactions of HBr with chain propagating or branching radicals such as H and OH which lead to less reactive species. Moreover HBr can play a role in the mechanisms of ozone depletion by bromine compounds in the atmosphere, which have been reviewed recently [4,5]. The ClO_Y radicals (Cl, ClO) and BrO_Y radicals (Br, BrO) can destroy ozone via catalytic cycles and HBr represents a temporary sink of Br atoms, which probably react with HO₂ and perhaps also with $H_2CO[6,7]$. The efficiency of this sink depends on the rate of regeneration of Br atoms by the main process: $OH + HBr \rightarrow H_2O + Br$. Then the reactions of H and OH with HBr are key reactions in flame inhibition and in atmospheric processes and consequently, their rate constants have to be known with good precision. The survey of the values of the literature shows a discrepancy of about a factor of two at room temperature between the discharge flow-EPR technique and flash photolysis measurements.

The reactions of H and OH with HBr have been studied directly by Takacs and Glass [8] and Endo and Glass [9] using the discharge flow technique with EPR detection. The rate constants of these reactions have been recently redetermined respectively by Husain and Slater [10] for reaction of H with HBr and by Ravishankara et al. [11] for reaction of OH with HBr. The technique used in both cases was the flash photolysis—resonance fluorescence. Then it was interesting to re-investigate these reactions In the present work, the discharge flow method was used but the parameters which appear to limit the EPR—flow reaction technique in the measurement of high rate constants were considered with special care. Especially for reaction OH + HBr, the sensitivity of the EPR analysis and the time resolution were higher than those used in ref. [8].

2. Experimental

The apparatus (fig. 1) has been described recently [12,13]. A Varian E112 EPR spectrometer equipped with an E235 large-access cylindrical cavity (24.5 mm i.d) was used for the gas-phase detection of atoms and diatomic radicals. The cavity was crossed by an all teflon reactor pumped by a 180 m³/h rotary pump giving a mean flow velocity of 50 m/s at a pressure of ≈ 0.5 Torr in the reaction zone. As has been noticed in previous works, such a flow speed



Fig 1. Diagram of the apparatus.

was necessary to spread the reaction zone over a distance long enough to reduce convolution effects of the species concentration signal by the absorption function of the cavity. The majority of the absorption was achieved in a 3 cm length and for the rate constants measured, the reaction zone usually extended 15-30 cm for a 90% consumption of the reactant H or OH. The pressure drop due to viscosity was another important limitation due to the high flow velocity of gases. The Poiseuille law applied to helium gave a pressure drop of 5×10^{-3} Torr/cm. The pressure was measured at different points along the reaction zone by means of a pressure transducer (MKS baratron) and the average value taken. The reactants were introduced into the reactor by means of sliding injectors. The inner tube used for the introduction of HBr was terminated by a multiholed sphere to produce a faster mixing of gases The intermediate tube was used for pressure measurements and for the introduction of NO₂ during OH experiments. The H atoms were generated in a microwave discharge (2450 MHz) in H₂ highly diluted by helium. Helium was passed through a liquid-nitrogen trap to remove impurities which produce H and O atoms in the discharge. HBr (Matheson cylinder) was distilled before being stored and diluted by argon in a 10 l bulb. No difference was noticed in the results with and without distillation of HBr.

Kinetic data and flow-rate parameters were processed on line by a 32K microcomputer (PET Commodore). The pressure drops from the bulbs were taken from digitalized pressure transducers (Membranovac Sogev) during experiments. The EPR signal could be processed in different ways, by double integration or by calculating the first moment of the derived recorded curves. Absolute concentrations of H and OH were obtained by comparison to reference spectra of respectively O_2 (E line J = 2, $M_J = 1 \rightarrow 2, 2$) and NO (D line $J = 3/2 - 1/2, 1 \rightarrow 1/2, 1$) as described by Westenberg [14]. Absolute concentrations of H and OH were measured before and after HBr had flowed in the reactor for each recorded decay curve. A difference in the two measurements observed in some experiments due to a change in the flow parameters or of the surface coating conditions led to the rejection of the kinetics. Rate constants were calculated directly after each experiment.

3. Results and discussion

3.1. Reaction (1): $H + HBr \rightarrow H_2 + Br$

Measurements were achieved under pseudo-firstorder conditions with $[HBr]_0 \gg [H]_0$, leading to the following equation: $\ln([H]_0/[H]) = k_1 [HBr]_0 t$. $([H]_0 \text{ and } [HBr]_0$ represent the initial concentration of the reactants [H] the concentration of H atoms at reaction time t.) The following initial conditions were used: $[H]_0 = (4-5.5) \times 10^{12} \text{ cm}^{-3}$ with $[HBr]_0$ ranging from 6.4×10^{13} to $2.1 \times 10^{14} \text{ cm}^{-3}$ corresponding to initial ratios ranging from 14 to 46. Higher ratios of concentrations were not used to avoid the convolution phenomenon as mentioned in section 2. Lower ratios were not used to prevent pressure-drop corrections and to satisfy the pseudofirst-order conditions.

Experimental pseudo-first-order rate constants



Fig. 2. Reaction H + HBr \rightarrow H₂ + Br: least-squares plot of the apparent first-order rate constant versus [HBr]₀ concentration: $k_1 = (6.3 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_{1(0)} = 15 \text{ s}^{-1}$.

were corrected for diffusion from the classical formula. $k_1 = k \exp[1 + k \exp(D_{H/He}/\bar{v}^2)]$. Using the diffusion coefficient of H in helium reported by Villermaux and Chery [15] $(D_{H/He} = 2.68 \text{ cm}^2/\text{s at}$ 1 atm) or Khouw et al. [16] $(D_{H/He} = 2.37 \text{ cm}^2/\text{s}$ at 1 atm) led to a non-negligible correction on the experimental rate constant (from 7 to 19% at $\bar{v} =$ 5000 cm/s).

The rate constant of reaction (1) was then calculated from the slope of the straight line: $d\{ln([H]_0/[H])\}/dt = f([HBr]_0)$ (fig. 2) by means of a leastsquares program. The following result was found for 30 experiments:

 $k_1 = (6.3 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$

with an intercept of 15 s^{-1} and a correlation coefficient of 0.96. No particular signification such as wall recombination of H atoms was attributed to the value of the intercept since it is low and within the standard error range.

The present value of k_1 can be compared with previous ones also obtained at room temperature. The EPR values obtained successively by Takacs and Glass [8] and Endo and Glass [9] were (3.4 ± 0.8) $\times 10^{-12}$ and $(3.71 \pm 0.14) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. However a higher value, $(6.0 \pm 0.1) \times 10^{-12}$, was recently obtained by Husain and Slater [10] by the flash photolysis—resonance fluorescence method. The present determination of $(6.3 \pm 0.5) \times 10^{-12}$ is in excellent agreement with this last value. Husain and Slater also studied the reactions of H with DBr and D with HBr and DBr and they found rate constants higher by about a factor of 2 than those of Endo and Glass. They attributed the divergence in the results to the poor spatial or time resolution in the EPR experiments. The analysis distance in the EPR large-access cavity which is 3-4 cm can be significant compared to the reaction length for fast decay rates and low flow velocities.

Takacs and Glass [8] used high decay rates of H atoms (600–1300 s⁻¹) with low flow velocities (\approx 13 m/s). Under these conditions, the maximum reaction distance was low (\approx 7 cm) compared to the analysis one, and the corresponding poor time resolution could explain the low value obtained for k_1 . However, in the second investigation by Endo and Glass [9], with lower decay rates (350–500 s⁻¹), higher flow velocities (\approx 18 m/s) and consequently higher maximum reaction distance (20 cm), no change was observed in k_1 Then it does not seem that the lower values obtained for k_1 can be mainly explained by the poor time resolution in the EPR measurements.

In the present work, with decay rates of 400– 1500 s⁻¹, flow velocities of 50 m/s and reaction distances up to 20 cm, the time resolution of EPR should not have any influence on k_1 measurements. Moreover, the absorption curve of the cavity, established by axially moving a small DPPH sample showed that 90% of absorption occurred over 2.5 cm, which is lower than previous measurements in a quartz reactor, giving better spatial resolution in the present work.

So no evident explanation can be proposed for the lower value of refs. [8,9] compared to the flashphotolysis value and the present one. Considering the EPR measurements, the major differences between the experimental conditions used in this work and the previous ones are: higher flow velocity, 50 m/s instead of 13-18 m/s, higher reaction distances as mentioned above, higher [HBr]₀/[H]₀ ratios, 14-46 instead of 2.5-9, and higher range of [HBr]₀, [HBr]_{0.max}/[HBr]_{0,min} = 3.3 against 2.2 in ref. [8] and 1.4 in ref. [9]. It appears that our experimental conditions are more suitable to obtain a better precision in k_1 measurements but the conditions of ref. [9] appear also to be correct to give a reasonable value of k_1 . A last difference concerns the nature of the Volume 78, number 3

surface of the reactor which is teflon in the present work and halocarbon wax in refs. [8,9], which could affect the wall processes. However both kinds of walls seem suitable to prevent wall effects and no evidence for such effects was noticed in the present work and in the previous ones.

3.2. Reaction (2) $OH + HBr \rightarrow H_2O + Br$

For this study, OH radicals were generated by the fast reaction

H + NO₂ \rightarrow NO + OH, (3) $k_3 = 1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$

NO₂ was used in excess compared to H atoms in order to get a total consumption of H atoms before HBr was injected in the reactor In preliminary experiments, the yield of production of OH radicals by reaction (3) was measured. It was first verified that there was agreement between the relative consumptions of H and NO₂. For $[H]_0 = 3.96 \times 10^{13}$ cm⁻³ and $[NO_2]_0 = 3.5 \times 10^{13}$ cm⁻³ the following ratio was found. $[NO_2]_{cons}/[H]_{cons} = 1.14$. This is in agreement with the fact that for high enough concentrations, this ratio ranges from 1 to 1.5 as a result of secondary reactions initiated by the homogeneous combination of OH radicals which is not negligible [16]. Besides with $[NO_2]_0 = 10[11]_0$, the



Fig. 3. Reaction OH + HBr \rightarrow H₂O + Br: least-squares plot of the apparent first-order rate constant versus [HBr]₀ concentration: $k_2 = (9.2 \pm 0.7) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_{2(0)} = 59 \text{ s}^{-1}$.

yield of OH radicals was found to never exceed 50% of H reacted from EPR analysis after a 2×10^{-3} s reaction time. After the production zone for OH radicals the homogeneous recombination becomes negligible due to low OH concentrations and the wall recombination of OH was experimentally found to be negligible on the teflon surface.

Kinetic studies were made with the following range of initial conditions of reactant concentrations: $[OH]_0 \approx 1.6 \times 10^{11} \text{ cm}^{-3}$ and $[HBr]_0$ ranging from 1.06×10^{13} to $1.12 \times 10^{14} \text{ cm}^{-3}$. The $[HBr]_0/$ $[OH]_0$ ratio was consequently varied from 66 to 700. The experimental data were corrected for diffusion effects using the coefficient of diffusion of atomic oxygen in helium given by Yolles and Wise [17] who found $D_{O/He} = 0.73 \text{ cm}^2/\text{s}$ at 1 atm. This diffusion coefficient was corrected for OH and the value 507 cm²/s taken at a pressure of 1 Torr. By fitting by a least-squares program the curve d{ln([OH]_0/[OH])}/ dt = f([HBr]_0), the following results were obtained from 25 experiments

$$k_2 = (9.2 \pm 0.7) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

 $k_{2(0)} = 59 \text{ s}^{-1}.$

The correlation coefficient was 0.993 and the standard error 26 s⁻¹. The value 59 s⁻¹ found for the intercept is not totally negligible as it is outside of the standard error domain. Since no consumption of OH radicals was measured in the absence of HBr along the reaction zone, we must consider that a wall reaction of OH radicals occurs with adsorbed HBr. The curve d{ln ([OH]₀/[OH])}/dt = f([HBr]₀) being a straight line, we admit that this phenomenon was constant over the whole range of HBr concentrations used. However the value of $k_{2(0)}$ is low compared to the measured decay rates and the process corresponding to $k_{2(0)}$ even if it would be partly homogeneous, would have a negligible effect on k_2 .

Only two direct measurements of k_2 have been published. By the discharge flow EPR technique, Takacs and Glass [8] obtained $k_2 = (5.1 \pm 1) \times 10^{-12}$ at room temperature. More recently by the flash photolysis—resonance fluorescence method, Ravishankara et al. found $k_2 = (1.19 \pm 0.14) \times 10^{-11}$ with no effect of temperature over the range 249-416 K. As for reaction (1) our value of k_2 differs by nearly a factor of 2 with the EPR measurement but is in good Volume 78, number 3

agreement with the flash photolysis determination. In their discussion, Ravishankara et al. proposed two possible reasons to explain the discrepancy between their results and those of Takacs and Glass. They first considered a possible error on [HBr] determination due to easy wall adsorption of HBr. In their study, they eliminated this source of error from measurements of [HBr] by UV absorption. Besides a systematic error in [HBr] measurements in the work of Takacs and Glass seems also unlikely if we consider that the rate constant found for the slower reaction of O with HBr studied also by EPR is in agreement with recent determinations [18,19]. Ravishankara et al. considered as a second possible source of discrepancy, the reaction of OH with a water-HBr complex which could occur in their system although they minimized this effect. As they pointed out, this phenomenon would be negligible in the EPR flow reactor where no H_2O is used to produce OH radicals. To prevent this effect, our reactor was dried by flowing BBr₃ before doing experiments to eliminate H₂O which is always present, adsorbed on the walls. The agreement between our value of k_2 and that of Ravishankara seems to demonstrate that the effect of a H_2O -HBr complex is probably minor.

The lower value of Takacs and Glass was obtained with high overall decay rates of OH ($1300-2400 \text{ s}^{-1}$) for low flow velocity (1300 cm/s); this corresponded to a maximum reaction distance of 5 cm, giving poor time resolution for EPR analysis. In the present work, where the decay rates are lower ($100-1060 \text{ s}^{-1}$) and the flow velocities higher (5000 cm/s), the higher reaction distance (up to 30 cm) gave a much better time resolution which could explain the difference between the two EPR works. Moreover, in ref. [8] the correction of k_2 for axial diffusion is not mentioned. If this correction had not been taken into account, k_2 should be increased by some ten percent, but k_2 would still remain low compared to our value and that of ref. [11].

4. Conclusion

The re-investigation of the reactions of H and OH with HBr at room temperature, has led to rate-constant determinations in agreement with recent values obtained by the flash photolysis—resonance fluorescence method, but somewhat higher than previous measurements by the EPR method. Especially for the reaction of OH with HBr, the higher value obtained in the present work could be explained by the better tume resolution in kinetic measurements.

For stratospheric application, the higher value obtained for k_2 confirms that HBr would be a much less efficient sink for Br atoms than HCl is for Cl atoms, as previously mentioned [11]. That increases the efficiency of ozone depletion by bromine compounds.

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