Discharge Flow Kinetic Study of the Reactions of NO₃ with Br, BrO, HBr, and HCI

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The reactions of NO3 with Br, BrO, HBr, and HCl have been studied at 298 K by using the discharge-flow EPR method. In the study of the reactions of NO₃ with Br and BrO, where NO₃ and Br or BrO were flowed separately in the presence of excess NO₃, the following rate constants were found: $k_1 = (1.6 \pm 0.7) \times 10^{-11}$ for NO₃ + Br \rightarrow NO₂ + BrO (1) and $0.3 \times 10^{-12} \le k_3 \le 3 \times 10^{-12}$ for NO₃ + BrO \rightarrow Br + NO₂ + O₂ (3). Units are cm³ molecule⁻¹ s⁻¹. For the reactions NO₃ + HCl \rightarrow products (6) and NO₃ + HBr \rightarrow products (7), the upper limits $k_6 \le 5 \times 10^{-17}$ and $k_7 \le 1 \times 10^{-16}$ were obtained.

Introduction

Due to the key role played by the NO₃ radical in the nighttime atmosphere, its reactions have been extensively studied in recent years. Many studies have been concerned with the reactions of NO₃ and organic molecules (ref 1 and references cited therein; ref 2 and 3); several reactions of NO₃ with inorganic molecules have also been investigated.⁴⁻⁶ The reactions of NO₃ with the following free radicals have also been recently studied: F,² Cl,^{5,7-9} ClO,⁸ OH,^{10,11} HO₂,^{10,12} and H.¹¹ These reactions are not directly relevant to atmosphere, except for the reaction of NO_3 with HO_2 , as previously discussed, ¹⁰ but they do occur in chemical systems used for studying atmospheric reactions of NO₃. In addition to assisting the interpretation of laboratory investigations of the atmospheric reactions of NO₃, studies of the NO₃ + free radical reactions aim to improve the knowledge of the basic reactivity of the NO₃ radical.

With this aim and as a continuation of our previous studies of the reactions of NO₃ with Cl, OH, and HO₂,^{9,10} we have investigated for the first time the reactions of NO3 with Br and BrO radicals. We also report studies of the reactions of NO3 with HCl and HBr. The reaction NO₃ + HBr was recently suggested to be a possible Br atom source during nighttime in the antarctic stratosphere.¹³ There is a link between the studies of this reaction and the reactions of NO₃ with Br and BrO, since these latter reactions are potential secondary steps of the reaction $NO_3 + HBr$. These reactions are also being studied at the same time in Mainz¹⁴

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by the modulated photolysis method, and the results should be published soon.

Experimental Section

The discharge-flow EPR apparatus used for the study of NO₃ reactions has been described in detail elsewhere.^{9,10} The reactor, shown in Figure 1, consisted of two axial tubes and a side arm. The flow tube, made of quartz, is 2.4 cm i.d. and 80 cm long. The sliding injector was 0.9 cm o.d. and 0.7 cm i.d. The reactor was coated with halocarbon wax (Halocarbon Products wax 12.00) to minimize the wall loss of the radicals NO₃, Br, and BrO.

NO₃ radicals were produced in the side arm by the fast reaction $F + HNO_3 \rightarrow HF + NO_3$.⁹ F atoms were generated by the microwave discharge dissociation of a flow of CF₄ diluted in helium. As HNO₃ was in excess over F atoms, all F atoms were removed in the side arm.

Br or BrO radicals were flowed into the main tube of the reactor through the sliding injector. Br atoms were produced by microwave dissociation of a flow of Br₂ in He. BrO radicals were also produced in the sliding injector by the addition of O₃ to Br atoms via the reaction

$$Br + O_3 \rightarrow BrO + O_2$$

The absolute concentration of NO₃ in the reactor was determined by chemical titration using an excess of NO over NO₃, monitoring the NO consumption by EPR. The validity of this method has been demonstrated previously.⁹ The deviation of the stoichiometry of 1:1 for the $NO + NO_3$ reaction, as a result of secondary chemistry in the NO3 source, was quantified by computer simulation:

$$F + HNO_3 \rightarrow HF + NO_3$$

 $F + NO_3 \rightarrow FO + NO_2$
 $FO + NO \rightarrow F + NO_3$

This deviation was always found to be less than 10% for the [HNO₃]/[F] ratios used here.

The Br atoms and BrO radicals were monitored by EPR in the gas phase. The absolute concentrations of Br atoms were determined by using O_2 as the reference as described by Westenberg.¹⁵ BrO radical concentrations were determined by titration of Br atoms via the reaction NO + BrO \rightarrow NO₂ + Br. The concentrations of Br and BrO for an S/N = 1 were respectively 5×10^{10} and 1×10^{11} cm⁻³.

The linear flow velocity and pressure in the reactor were typically in the range 18-30 m/s and 0.7-0.8 Torr, respectively. The

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Figure 1. Discharge flow apparatus.



Figure 2. Plot of decay in Br concentration versus time for the determination of the rate constants for the reactions $NO_3 + Br \rightarrow NO_2 + BrO$ (1) and $NO_3 + BrO \rightarrow NO_2 + Br + O_2$ (3). Initial conditions; $[NO_3]_0 = 4.29 \times 10^{13} \text{ cm}^{-3}$, $[Br]_0 = 4.31 \times 10^{12} \text{ cm}^{-3}$. The dots are the experimental results and the solid lines [1], [2], and [3] were obtained from computer simulation using $k_3 = 0.7 \times 10^{-12}$ and $k_1 = 1.4 \times 10^{-11}$ (best fit), 0.7×10^{-11} and 2.8×10^{-11} for curves [1], [2], and [3], respectively.

pressure was measured 10 cm upstream of the EPR cavity by using an MKS baratron capacitance manometer.

 HNO_3 was prepared by distilling a mixture of NaNO₃ and concentrated H_2SO_4 . O₃ was generated from a commercial ozonizer and stored for subsequent use in a darkened glass flask. The other gases and liquid Br_2 used in this work were of the best commercial purity available.

Results

1. Reactions of NO₃ with Br and BrO. The reaction of NO₃ with Br was studied with an excess of NO₃ over Br. The absolute concentration of NO₃ was measured in the absence of Br atoms before and after each experiment by the titration method described in the previous section. The initial concentration ranges used were $(0.90-6.37) \times 10^{13}$ cm⁻³ for NO₃ and $(1.26-8.79) \times 10^{12}$ cm⁻³ for Br atoms.

The decay of the Br atom concentration as a function of reaction time was monitored by EPR and a typical curve obtained is shown in Figure 2. The kinetic treatment of the Br decay curves showed evidence for regeneration of Br atoms by secondary reactions. One possible source of Br atoms is the reaction 2a of the self-combination of the BrO radicals produced in the initial step:

$$NO_3 + Br \rightarrow BrO + NO_2$$
 (1)

$$BrO + BrO \rightarrow 2Br + O_2$$
 (2a)

$$\Rightarrow Br_2 + O_2 \tag{2b}$$

However, a computer simulation using these reactions did not yield a good fit between calculated and experimental Br decay

TABLE I: Determination of the Rate Constant for the Reaction NO_3 + Br \rightarrow BrO + NO_2 ; Mechanism Used in the Computer Simulations

reaction	k(298)		
(1) $NO_3 + Br \rightarrow BrO + NO_2$	variable		
(2a) $BrO + BrO \rightarrow 2Br + O_2$	2.3×10^{-12a}		
(2b) $BrO + BrO \rightarrow Br_2 + O_2$	4.4×10^{-13a}		
(3) $NO_3 + BrO \rightarrow Br + NO_2 + O_2$	variable		
(4) $Br + wall \rightarrow products$	$2-10^{b}$		

^{*a*} From ref 4, in cm³ molecule⁻¹ s⁻¹ units. ^{*b*} In s⁻¹ units.

TABLE II: Rate Constant Determination for the Reaction NO₃ + Br \rightarrow BrO + NO₂ (1) ($k_1 = (1.6 \pm 0.5) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ at 298 K)

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 $[NO_3]_0,$ 10 ¹³ cm ⁻³	$[Br]_0,$ 10 ¹² cm ⁻³	$k_1,$ 10 ⁻¹¹ cm ³ molecule ⁻¹ s ⁻¹	
0.90	1.26	1.95 ± 0.15	
1.10	2.42	1.94 ± 0.15	
1.27	1.54	1.92 ± 0.15	
1.92	1.96	1.33 ± 0.05	
2.32	2.38	1.69 ± 0.12	
2.40	4.11	1.62 ± 0.04	
3.48	4.84	1.15 ± 0.05	
3.62	2.53	1.55 ± 0.16	
4.15	4.56	1.65 ± 0.09	
4.29	4.31	1.39 ± 0.05	
4.55	5.6	1.51 ± 0.09	
5.64	6.61	1.34 ± 0.04	
6.37	8.79	1.31 ± 0.08	

curves, indicating that an additional production of Br atoms occurred. The additional reaction was considered to be

$$NO_3 + BrO \rightarrow NO_2 + Br + O_2$$
(3)

This route is thermochemically favorable ($\Delta H = -12.4 \text{ kcal/mol}$; the alternative path giving BrOO and NO₂ is equivalent because BrOO has a very short lifetime: the bond energy Br-O₂ has been estimated¹⁶ to be 1 kcal/mol). Reactions 1 + 3 are similar to the sequence previously observed¹⁰

$$NO_3 + OH \rightarrow NO_2 + HO_2$$
$$NO_3 + HO_2 \rightarrow NO_2 + OH + O_2$$
(4)

where OH was regenerated by the secondary step between NO_3 and the radical produced in the first reaction.

As a result of the occurrence of secondary step, the rate constant of the reaction of NO₃ with Br was determined from computer simulation of the mechanism reported in Table I by fitting the calculated and experimental decay curves of Br atoms. The results obtained from 13 experiments are given in Table II where the error on each k_1 value corresponds to 95% confidence limits obtained in the best fit procedure. The resulting mean value of k_1 is

$$k_1 = (1.6 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

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Figure 3. Plot of decay in Br concentration for the same experiment as shown in Figure 2. The computed curves [1], [2], and [3] were obtained by using $k_1 = 1.4 \times 10^{-11}$ and $k_3 = 0.7 \times 10^{-12}$ (best fit), 2.8×10^{-12} , and 0.7×10^{-13} for curves [1], [2], and [3], respectively.

The error represents two standard deviations. Values of k_3 were also derived by the same procedure leading to $k_3 = (0.7 \pm 0.4) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 298 K. The error is one standard deviation. The error on k_3 is much higher than for k_1 due to the lower sensitivity of the Br kinetics to k_3 as compared to k_1 . This difference in sensitivity of the Br kinetics to k_1 and k_3 is illustrated in Figures 2 and 3, where comparable changes of the Br decay curves are obtained under the following conditions: $k'_1 = 2k_1$ and $0.5k_1,k_3$ unchanged (Figure 2); $k'_3 = 4k_3$ and $0.1k_3,k_1$ unchanged (Figure 3).

Another set of experiments was carried out, monitoring directly both BrO and Br. The initial Br atom concentrations were relatively high $(8-10 \times 10^{12} \text{ cm}^{-3})$ in order to have a sufficient sensitivity for the EPR detection of the BrO radicals. A typical set of results obtained is shown in Figure 4 where the initial concentration of NO₃ and Br were respectively 3.93×10^{13} and 9.8×10^{12} cm⁻³. The rate constants k_1 and k_3 were calculated from the computer simulation of such curves, using the reaction parameters of Table II. In these computations, the BrO + BrO reaction was not negligible as in the first series of experiments. The calculated rate constant k_3 was very sensitive to k_{2a} . Calculations were undertaken, using two sets of values for k_{2a} and k_{2b} at 298 K: (i) the recommended values of the NASA Panel,⁴ $k_{2b} = 2.3 \times 10^{-12}$ and $k_{2b} = 4.4 \times 10^{-13}$, which are the averages between the determinations of Clyne and Watson¹⁷ and Sander and Watson;¹⁸ (ii) $k_{2a} = 3.4 \times 10^{-12}$ and $k_{2b} = 6.6 \times 10^{-13}$ corresponding to the determination of k_{2b} by Cox et al.,¹⁹ which is 50% higher than the NASA recommendation. For the experiment shown in Figure 4, fits using the two sets of values yield respectively $k_1 = 1.7 \times 10^{-11}, k_3 = 2.4 \times 10^{-12}$ and $k_1 = 1.6 \times 10^{-11}, k_3 =$ 1.0×10^{-12} . In conclusion, the value of k_1 obtained by fitting the mechanism to the data obtained in this experiment is insensitive to the values of k_{2a} and k_{2b} used. This is not the case for the value of k_3 determined by this procedure. It appears that using k_{2a} and k_{2b} from Cox et al. yields a value for k_3 which is within experimental error in agreement with the determination of k_1 described above.

A third series of experiments was carried out to determine k_3 in which NO₃ was flowed into the reactor together with BrO instead of Br atoms. As already described in the Experimental Section, NO₃, in excess over BrO, was produced in the side-arm tube of the reactor and BrO in the axial internal one. O₃ was added in excess over Br atoms to produce BrO, in order to avoid



Figure 4. Plot of Br and BrO kinetics for the determination of the rate constants for the reactions $NO_3 + Br \rightarrow NO_2 + BrO$ (1) and $NO_3 + BrO \rightarrow NO_2 + Br + O_2$ (3). Initial conditions: $[NO_3]_0 = 3.93 \times 10^{13}$ cm⁻³, $[Br]_0 = 9.8 \times 10^{12}$ cm⁻³. The circles and triangles are the experimental results and the solid lines were obtained from computer simulation using for k_{2a} and k_{2b} the following values: 2.3×10^{-12} and 4.4×10^{-13} for curves (1), 3.4×10^{-12} and 6.6×10^{-13} for curves (2). The corresponding k_1 and k_3 values obtained from the best fit procedure were respectively 1.7×10^{-11} and 2.2×10^{-12} (curves (1)) and 1.6×10^{-11} and 1×10^{-12} (curves (2)).

a direct reaction of Br with NO₃. The O₃ concentration in the reactor was determined from the measurement of the O₃ flow rate which was corrected from the O₂ impurity measured by EPR. The following initial concentration of reactants were used: $[NO_3]_0 = (1.0-4.6) \times 10^{13}$, $[BrO]_0 = (1.4-2) \times 10^{12}$ cm⁻³, and $[O_3]_0 = (1.8-4.5) \times 10^{14}$ cm⁻³.

The EPR kinetics of BrO did not show any measurable consumption of this radical, which confirmed the rather high ratio k_1/k_3 observed in the previous experiments. The fast regeneration of BrO was not only due to reaction 1 but also to the reaction

$$Br + O_3 \rightarrow BrO + O_2$$
 (5)

since excess O₃ was used $(k_5 = 1.2 \times 10^{-12} \text{ at } 298 \text{ K}^4)$.

In these experiments k_3 could be calculated from the EPR measurement of the stationary Br atom concentration. Assuming that Br atoms attain a stationary state, k_3 was given in this system by the equation

$$k_3 = \{([Br]/[BrO])(k_1[NO_3] + k_5[O_3]) - 2k_{2a}[BrO]\}/[NO_3]$$

The self-combination reaction of BrO (2a) was in fact negligible at the BrO concentrations used. And for the initial concentrations of NO₃, BrO, and O₃ mentioned above, the stationary Br atom concentration was similar to the EPR detection limit. Consequently, an upper limit for k_3 can be estimated from these measurements:

$$k_3 \le 3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

This upper limit is consistent with the values obtained in the two first series of experiments. From the three series of experiments, the preferred value of k_3 lies in the range

$$0.3 \times 10^{-12} \le k_3 \le 3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

2. Reactions of NO_3 with HCl and HBr. Reaction between NO_3 and HCl or HBr may be expected at room temperature because reaction 6 is nearly thermoneutral and reaction 7 exothermic:

$$NO_3 + HCl \rightarrow HNO_3 + Cl \qquad \Delta H = 1.7 \pm 1 \text{ kcal/mol} (6)$$

$$NO_3 + HBr \rightarrow HNO_3 + Br \qquad \Delta H = -13.5 \pm 1 \text{ kcal/mol} (7)$$

The uncertainty in the heats of reaction arises from the error on the recommended heat of formation of NO₃:⁴ $\Delta H = 17 \pm 1$ kcal/mol.⁴ The use of the most recent determination of $\Delta H_f(NO_3)$

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TABLE III: Rate Constants Available at Room Temperature for Reactions of NO3 with Free Radicals^a

	k(room temperature), cm ³ molecule ⁻¹ s ⁻¹	ΔH	ref	
$H + NO_3 \rightarrow OH + NO_2$	$(1.1 \pm 0.6) \times 10^{-10}$	-51.9	11	
$O + NO_3 \rightarrow O_2 + NO_2$	$(1.7 \pm 0.6) \times 10^{-11}$	-68.7	С	
$OH + NO_3 \rightarrow HO_2 + NO_2$	$(2.6 \pm 0.6) \times 10^{-11}$	-15.4	10	
$HO_2 + NO_3 \rightarrow OH + NO_2 + O_2$	$(3.6 \pm 0.9) \times 10^{-12}$	-2.8	10	
$HO_2 + NO_3 \rightarrow HNO_3 + O_2$	$(9.2 \pm 4.8) \times 10^{-13}$	-52.3	10	
$F + NO_3 \rightarrow FO + NO_2$	3×10^{-11}	-2.1	2	
$FO + NO_3 \rightarrow products$	1×10^{-12}	-16.1^{b}	2	
$Cl + NO_3 \rightarrow ClO + NO_2$	$(2.6 \pm 0.5) \times 10^{-11}$	-13.6	9	
$ClO + NO_3 \rightarrow products$	4×10^{-13}	-4.6ª	8	
$Br + NO_3 \rightarrow BrO + NO_2$	$(1.6 \pm 0.5) \times 10^{-11}$	-5.8	this work	
$BrO + NO_3 \rightarrow Br + NO_2 + O_2$	$(0.3-3) \times 10^{-12}$	-12.4	this work	

^a The heats of reaction, ΔH , are in kcal/mol. ^b ΔH has been calculated for the route XO + NO₃ \rightarrow X + NO₂ + O₂ (X = F, Cl). For reactions of NO3 with OH, HO2 and Cl, the rate constants reported come from our own work. They reasonably agree with those of ref 5, 7, 8, 11, and 12. ^c This result is from R. P. Wayne, private communication.

= 15.4 \pm 0.7 kcal/mol²⁰ leads to ΔH values of 3.3 \pm 0.7 and -11.9

study and k_{2a} and k_{2b} from ref 4. The following upper limit was obtained for k_7 :

 $k_7 \le 1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$

Discussion

Reactions $NO_3 + Br$ and BrO. The results presented here on the reactions of NO₃ with Br and BrO increase our knowledge of the reactions of NO₃ with free radicals. These reactions are listed in Table III, with their rate constants at room temperature and their heats of reaction. Except for the channel of the reaction of HO₂ with NO₃ which produces HNO₃ and O₂, these radical-radical reactions of NO3 appear to proceed via an O atom transfer mechanism where NO₃ is converted to NO₂. Examination of the rate constants of the reactions of Table III does not show evidence for a special trend of reactivity. This may be explained by the fact that most of these reactions would be indirect, processing through a long-lived intermediate, with a net rate constant depending on the complex combination of the rates of the individual steps.

Considering the reactions of NO_3 with halogenated radicals, it appears that the rate constants for the $NO_3 + X$ and $NO_3 +$ XO reactions are comparable, with generally a much lower reactivity of XO compared to X (reactions $NO_3 + X$, k = (1.6-3.0)× 10⁻¹¹; NO₃ + XO, $k = (0.3-3.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).

Reactions $NO_3 + HCl$ and HBr. Our upper limit of 5×10^{-17} for the rate constant of the reaction between NO3 and HCl is compatible with the upper limit of 7×10^{-18} recently obtained in a nonphotolytic cell with FTIR kinetic analysis.²¹

The present upper limit and our previous kinetic data on the reverse reaction Cl + HNO₃ can be used to calculate a lower limit for the equilibrium constant of these two reactions:

$$NO_3 + HCl \rightleftharpoons Cl + HNO_3$$
 (6, -6)

The value $k_{-6} = 2 \times 10^{-17}$ was found at room temperature from extrapolation of data obtained at higher temperatures in a discharge-flow system.²² This value is compatible with our further room temperature experiments which yielded $k_{-6} \le 5 \times 10^{-16.23}$ Therefore, from $k_6 \le 5 \times 10^{-17}$ and $k_{-6} = 2 \times 10^{-17}$ we can derive $K = k_6/k_{-6} \le 2.5$. This data is in agreement with the value K = 0.15 obtained from thermochemical data ($\Delta H_{f,298} = 17, -22.07$, 28.9, and -32.3 kcal/mol, $S^{\circ}_{298} = 60.4$, 44.6, 39.5, and 63.7 cal/mol for NO₃, HCl, Cl, and HNO₃, respectively. The thermochemical calculation yields K = 0.01 if the value 15.4 kcal/mol is taken for $\Delta H_{\rm f}(\rm NO_3)$.

For the reaction $NO_3 + HBr$, there is not other room temperature data to be compared with ours, but some recent hightemperature data also obtained by the discharge-flow method²⁴

 \pm 0.7 kcal/mol for reactions 6 and 7, respectively. Reactions 6 and 7 have been studied under pseudo-first-order

conditions with an excess of HX (HCl, HBr) over NO₃. The NO₃ concentration was measured in the presence and absence of HX (NO₃ concentration was determined from the EPR measurement of the consumption of excess NO added upstream of the EPR cavity). No evidence for any reaction was observed.

A second method was used to investigate reactions 6 and 7. In this case halogen atoms were monitored by EPR to look for the possible X atom formation via the reaction sequence:

$$NO_3 + HX \rightarrow HNO_3 + X$$
 (I)

$$NO_3 + X \rightarrow NO_2 + XO$$
 (II)

$$NO + XO \rightarrow NO_2 + X$$
 (III)

Any X atom, produced in step I, would be rapidly converted into XO via reaction II. XO is reconverted into X by adding excess NO upstream of the EPR cavity. XO was indirectly analyzed in this manner because the EPR sensitivity is higher for X than for XO. Under these conditions the rate constant k_1 could be derived by fitting the experimental XO concentration with the calculated value obtained by a computer simulation of reactions I, II, and the following steps:

$$NO_3 + XO \rightarrow products$$
 (IV)

$$XO + XO \rightarrow \text{products}$$
 (V)

In the computations, $k_{\rm II}$, $k_{\rm IV}$, and $k_{\rm V}$ were held constant and $k_{\rm I}$ was varied.

For the reaction of NO₃ with HCl, the typical experimental conditions were $[NO_3]_0 = (5.9-7.8) \times 10^{13} \text{ cm}^{-3}$, $[HCl]_0 = (0.87-1.1) \times 10^{16} \text{ cm}^{-3}$, P = 2 Torr, and a reaction time of 0.07-0.13 s. Under these conditions, no Cl atoms could be detected yielding [Cl] = [ClO] $\leq 5 \times 10^{11}$ cm⁻³. The computer simulations involved the reactions

$$NO_3 + Cl \rightarrow NO_2 + ClO \tag{8}$$

$$NO_3 + ClO \rightarrow products$$
 (9)

$$ClO + ClO \rightarrow products$$
 (10)

The following rate constants were taken: $k_8 = 2.6 \times 10^{-11,9}$ $k_9 = 4.0 \times 10^{-13,8}$ and $k_{10} = 1.2 \times 10^{-14}$ cm³ molecule⁻¹ s^{-1,4} and the fitting procedure led to the following upper limit of k_6 :

$$k_6 \le 5 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

For the reaction of NO3 with HBr, experimental conditions very similar to those for reaction 6 were used: $[NO_3]_0 = (0.6-1.1)$ × 10^{14} cm⁻³, [HBr]₀ = (2.4–8.1) × 10^{15} cm⁻³, P = 1.6–2.5 Torr, and t = 0.05-0.07 s. Under these conditions no Br atoms could be observed, yielding $[Br] = [BrO] \le 10^{12} \text{ cm}^{-3}$. In the computer simulation, the values of k_1 and k_3 were taken from the present

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are consistent with our determination.

Atmospheric Implications. The data reported here improve our knowledge of the chemistry of halogen-containing species and oxides of nitrogen which play an important role in the stratospheric chemistry. NO₃ reaches its maximum concentration at night in the stratosphere because of its strong visible absorption, whereas Br and BrO concentrations are conversely at their high concentration during daytime. However, due to the low temperature in the stratosphere, N_2O_5 , which is formed at night in the equilibrium reaction between NO₂ and NO₃, is not rapidly decomposed at dawn but rather continues to release NO₃ throughout the day. Although it is not anticipated that the addition of the reactions of Br and BrO with NO3 to stratospheric models will significantly alter our understanding of the behavior of stratospheric O_3 , these reactions convert NO_3 to NO_2 . Due to the complex nature of stratospheric chemistry, a detailed analysis of the effect of the addition of these reactions to stratospheric chemistry must await more detailed modeling studies.

The reactions of NO₃ with HCl⁶ and HBr⁷ will be of negligible stratospheric importance. Reaction 7 was recently suggested as a potential route of HBr/Br conversion in the antarctic stratosphere during springtime.¹³ In addition to active chlorine, the active bromine produced by this route and by the reaction OH + HBr \rightarrow Br + H₂O would have contributed to form the ozone hole. But the present data shows that reaction 7 is too slow at stratospheric temperatures to be significant in the ozone hole chemical mechanism.

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Hg(³P) Photosensitized Chemistry of Ethyl Halides in Krypton Matrix

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The reaction of Hg atoms in the ³P state with the ethyl halides is studied in krypton matrix. The primary products result from molecular elimination, though the behavior of ethyl fluoride is different from that of ethyl chloride and bromide in that H_2 elimination is observed exclusively rather than the hydrogen halide elimination that predominates for the other ethyl halides. Some insertion of Hg into C-Cl and C-Br bonds occurs, a process absent in the gas-phase photochemistry.

Introduction

The reaction of group IIB metals in their lowest excited electronic state (³P) with a number of halogenated ethenes in cryogenic matrices has recently been reported, and a variety of reaction pathways has been observed. The sole product of the reaction of Hg, Cd, and Zn (³P) with 2-chloro-1,1-difluoroethylene has been shown to be a difluorovinyl metal chloride that results from the insertion of the excited metal atom into the C-Cl bond.¹ Insertion into C-Cl bonds, as well as molecular HCl and Cl₂ elimination, has been observed on Hg(³P) photosensitization of the three isomers of dichloroethylene in krypton matrix.² Most recently, we have reported hydrogen halide elimination and metal atom insertion for the reaction of ³P group IIB metal atoms with matrix isolated vinyl halides.³ (References 1-3 will hereafter be referred to as I-III, respectively.) We now present results of our studies on the reaction of $Hg(^{3}P)$ with ethyl halides in krypton matrix. These saturated analogues of the vinyl halides previously studied have significantly different electronic structures (no π system) and hence might be expected to access different photochemical pathways.

The ethyl halides, abbreviated EX (X = F, Cl, and Br), share a number of desirable features with the vinyl halides studied in III. Their gas-phase IR spectra, and in some cases matrix isolation spectra, are well-known, as are those of the anticipated products.⁴⁻⁸ The $Hg(^{3}P_{1})$ photosensitized chemistry of EF and ECl has already been investigated in detail in the gas phase.^{9,10} Ab initio calculations have also been employed to characterize hydrogen halide elimination from these species.^{11,12} In addition, careful study of the UV absorption spectra of the ethyl halides has revealed a great deal about their electronic structures.¹³⁻¹⁵ So, as with the vinyl halides, the ethyl halides present a nearly ideal series of molecules

with which to study the reactions of excited group IIB metal atoms in cryogenic solids.

Results of some studies with other alkyl halides, and the conditions under which they were obtained, will also be presented.

Experimental Section

The cryogenic apparatus, deposition technique, and FTIR spectroscopy have previously been described in I. Typically, 1-2 mmol of a premixed matrix gas/reactant sample at M/R = 100was deposited on a CsI substrate with a flow rate of 0.5-1.0 mmol h^{-1} . Krypton, which was used as the host in most experiments, was condensed at 20 K. The Ar and N₂ mixtures used in several experiments were deposited at 12 K. Spectra (0.5- or 0.25-cm⁻¹ resolution) were recorded and photolyses were conducted at 12 K. Atomic Hg was added to the matrix as described in I, by

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