## Kinetics of the Reaction of Iodine Atoms with HO<sub>2</sub> Radicals

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The rate coefficient  $(k_2)$  for the reaction of iodine atoms with HO<sub>2</sub> radicals,  $I + HO_2 \rightarrow HI + O_2$ , has been measured directly with use of the discharge-flow/EPR technique, and the molecular-modulation/UV-absorption spectroscopy technique. Discharge-flow measurements were made under pseudo-first-order conditions with iodine atoms in large excess over HO<sub>2</sub>. Molecular-modulation measurements were made with iodine atoms in excess over  $HO_2$ , but the I +  $HO_2$  reaction was occurring in competition with the self-reaction of HO<sub>2</sub>. The values of  $k_7$  determined at 298 K by these complementary methods agree within the combined experimental errors and provide a value of  $(3.8 \pm 1.0) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Further measurements made over the temperature range 283-353 K with the molecular-modulation technique allow recommendation of the following expression:  $k_7 = (1.47 \pm 0.63) \times 10^{-11} \exp(-(1090 \pm 130)/T)$ . The potential significance of this reaction as a sink for iodine in the troposphere and other aspects of tropospheric iodine chemistry are considered with a simple model of the atmospheric boundary layer.

#### 1. Introduction

The potential significance of iodine compounds in tropospheric photochemistry has received some attention in recent years.<sup>1-3</sup> Since iodine-containing molecules generally possess intense absorption spectra in the visible or near-ultraviolet, they are photolyzed efficiently in the lower atmosphere (e.g., marine boundary layer) to produce iodine atoms. The subsequent reaction of iodine atoms with O<sub>3</sub> to produce IO radicals occurs rapidly at O<sub>3</sub> levels typically observed in the boundary layer (e.g., after ca. 1 s for  $[O_3] = 40 \text{ ppb})$ :

$$I + O_3 \rightarrow IO + O_2 \tag{1}$$

IO is known to be converted back into iodine atoms efficiently by photolysis<sup>4,5</sup> or reaction with NO<sup>6,7</sup> or CH<sub>3</sub>SCH<sub>3</sub> (DMS).<sup>8,9</sup> This cyclic interchange of iodine atoms and IO radicals, which plays a dominant role in atmospheric iodine behavior, has no net chemistry if IO is photolyzed or reacts with NO (see discussions in ref 1 and 2). If IO reacts with DMS, however, production of CH<sub>3</sub>SOCH<sub>3</sub> (DMSO) results<sup>8,9</sup> together with removal of O<sub>3</sub>:

> $IO + DMS \rightarrow DMSO + I$ (2)

$$DMS + O_3 \rightarrow DMSO + O_2$$
 (1 + 2)

The reaction of IO with other trace species may result in their oxidation in a similar manner, with concurrent loss of  $O_3$ . The rate of an oxidation process of this type is governed by the concentration of iodine atoms and IO radicals in the atmosphere. This in turn is determined by the relative rates of production and removal of these species. Production of iodine atoms in the atmosphere can result from the photolysis of CH<sub>3</sub>I, which is a known constituent of the atmosphere, especially the marine boundary

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layer,<sup>10</sup> or other organic iodides.

$$CH_3I + h\nu \rightarrow CH_3 + I \tag{3}$$

Potential removal routes for iodine atoms or IO radicals involve the following reactions: ...

$$IO + NO_2 \xrightarrow{M} IONO_2$$
 (4)

$$IO + IO \xrightarrow{M} I_2O_2 \rightarrow attachment to particles$$
 (5)

$$IO + HO_2 \rightarrow HOI + O_2$$
 (6)

 $I + HO_2 \rightarrow HI + O_2$ (7)

followed by physical removal of IONO<sub>2</sub>, particulate iodine, HOI, or HI. Reactions 4 and 5 have been investigated,<sup>4,11,12</sup> but no kinetic data exist for the reaction of either iodine atoms or IO radicals with HO<sub>2</sub>.

The reactions of halogen atoms with HO<sub>2</sub> (X + HO<sub>2</sub>  $\rightarrow$  HX + O<sub>2</sub>) have been studied for F,<sup>13,14</sup> Cl,<sup>15</sup> and Br<sup>16</sup> and show a decreasing reactivity at room temperature (ca.  $5 \times 10^{-11}$ ,  $3.2 \times$  $10^{-11}$ , and  $0.2 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively). Since the preexponential factors are similar, the activation energies tend to increase along the series F to Br. For Cl, the alternative pathway forming ClO and OH is important at 298 K (k = 9.1 $\times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-115</sup>), whereas the analogous pathways for F and Br (and I) are significantly endothermic. The reactions of halogen atoms with  $HO_2$  have been reviewed in some detail by Mozurkewich<sup>17</sup> and recently by Toohey and Anderson.<sup>18</sup>

In this paper, we present the results of kinetic studies to investigate the reaction of iodine atoms with HO<sub>2</sub> radicals (reaction 7). Experiments were performed using both the dischargeflow/EPR technique and molecular-modulation/UV spectroscopy to make complementary, direct measurements of  $k_7$ .

#### 2. Experimental Section

2.1. Discharge-Flow Experiments. The experimental arrangement, first described in ref 19 and schematically represented

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Figure 1. Discharge-flow experimental arrangement.

in Figure 1, consisted of a quartz reactor (2.4-cm internal diameter), coated with halocarbon wax to reduce wall reactions. The reactor crossed the EPR large access cavity (Varian Model E235) associated with a Varian Model E112 EPR spectrometer. Iodine atoms and HO<sub>2</sub> radicals were generated separately in a reactor equipped with a double microwave discharge. Iodine atoms flowed into the quartz reactor through a side-arm tube located 55 cm upstream of the EPR cavity. HO<sub>2</sub> radicals entered through the central tube (9-mm outside diameter), which could be moved along the reactor axis. Iodine atoms were analyzed directly by EPR, whereas HO<sub>2</sub> radicals were monitored indirectly by converting HO<sub>2</sub> to OH by the rapid reaction 8 ( $k_8 = 8.3 \times 10^{-12} \text{ cm}^3$ 

$$NO + HO_2 \rightarrow NO_2 + OH$$
 (8)

molecule<sup>-1</sup> s<sup>-1</sup> at 298 K<sup>20</sup>). NO was added 10 cm upstream of the EPR cavity, at concentrations high enough to achieve total conversion of HO<sub>2</sub> to OH radicals, which were analyzed subsequently by EPR.

lodine atoms were produced by the fast reaction 9 ( $k_9 = 8 \times$ 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K<sup>21</sup>). Cl atoms were generated by microwave dissociation of Cl<sub>2</sub> highly diluted in helium. This

$$CI + ICI \rightarrow I + CI_2 \tag{9}$$

source was found to be more convenient than the microwave discharge of I<sub>2</sub>, which was checked in a first series of experiments. The presence of significant concentrations of undissociated I<sub>2</sub> in the reaction mixture was found to cause complications in the detection of HO<sub>2</sub>, due to the rapid reaction of I<sub>2</sub> with OH radicals, which prevented precise and reliable kinetic monitoring of HO<sub>2</sub>:

$$OH + I_2 \rightarrow products$$
 (10)

$$k_{10} = 1.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}^{22}$$

This effect was less important with unreacted ICl when reaction 9 was used as the source of iodine atoms, since the rate constant for the reaction of OH with ICl is significantly lower than that for reaction 10. The first measurement of k(OH + ICI) yielded a value of  $(2^{+2}_{-1}) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K,<sup>22</sup> while our recent determination was  $(1.1 \pm 0.1) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K.<sup>23</sup> Although kinetic measurements of the I + HO<sub>2</sub> reaction were possible with moderate excess of ICl over Cl, four kinetic experiments were also carried out using an excess of Cl atoms over ICl, in order to suppress the reaction of OH with ICl totally. Under these latter conditions, however, remaining Cl atoms had to be scavenged in order to eliminate the fast reaction with  $HO_2$ , which competed with reaction 7. This was achieved by adding C<sub>2</sub>H<sub>6</sub> to the system, which reacted rapidly with Cl atoms  $(k_{11} = 5.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}^{20}).$ 

$$Cl + C_2H_6 \rightarrow HCl + C_2H_5 \tag{11}$$

Additional EPR measurements indicated that Cl atoms were removed completely prior to injection of HO<sub>2</sub> into the main reactor and therefore caused no complications in the chemistry of HO<sub>2</sub>. The absence of Cl atoms also indicated that C2H5 radicals were no longer present, since they would react rapidly with undissociated Cl<sub>2</sub> to regenerate Cl atoms  $(k_{12} = 1.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K<sup>24</sup>):

$$C_2H_5 + Cl_2 \rightarrow C_2H_5Cl + Cl \tag{12}$$

Clearly, C2H5 radicals were removed by other reactions (e.g., with Cl atoms) and consequently did not interfere with the behavior of  $HO_2$ .

HO<sub>2</sub> radicals were produced by the following reaction sequence, with Cl atoms generated by microwave dissociation:

$$CI + CH_{3}OH \rightarrow CH_{2}OH + HCI$$
(13)

$$CH_2OH + O_2 \rightarrow HCHO + HO_2$$
 (14)

The reactor was pumped by means of 250 m<sup>3</sup> h<sup>-1</sup> Roots pump, allowing linear velocities of 15-23 ms<sup>-1</sup> at total pressures in the range 1.0-1.5 Torr.

All gases, except He and ICl, were stored in 10-L bulbs. Helium was flowed directly from the cylinder and ICl from the liquid maintained at 0 °C. The reactants used (He, NO, Cl<sub>2</sub>, ICl, C<sub>2</sub>H<sub>6</sub>,  $CH_3OH$ , and  $O_2$ ) had the best purity commercially available.

2.2. Molecular-Modulation Experiments. These experiments were performed in a 1.2-L quartz reaction vessel, which was surrounded by a jacket containing either ethanol or water, allowing temperature regulation of the vessel. During kinetics experiments, reagents, products, and transient species could be monitored in absorption at specific wavelengths in the UV-visible region, with use of deuterium or tungsten lamp source with dispersion and detection on a conventional monochromator (Spex 0.75 m)/ photomultiplier (EMI 9783B) arrangement. The absorption path length was 120 cm. Additional spectral measurements were made by dispersion of the monitoring beam on a 0.5-m spectrograph (B and M Spectronik) and detection on a 1024 channel photodiode array (Reticon), giving a spectral coverage of ca. 80 nm. The detector was coupled to a multichannel analyzer (Tracor Northern TN1710) allowing storage and manipulation of the data. Detailed descriptions of the reaction vessel and associated spectroscopic equipment have been given in previous publications.<sup>11,25,26</sup>

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HO<sub>2</sub> radicals were generated, as in the discharge flow experiments, by reaction sequence 13 followed by 14. Cl atoms were produced by the near-UV photolysis of  $Cl_2$  (310 <  $\lambda/nm$  < 400) with use of fluorescent black lights (Sankyo Denki FL405). The generation of iodine atoms was achieved by the photolysis of  $I_2$ in its intense visible band, using fluorescent gold lamps (Thorn EMI, 40 W) emitting over the wavelength range 500-700 nm  $(\lambda_{max} = 570 \text{ nm}):$ 

$$I_2 + h\nu \to I + I \tag{15}$$

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The photolysis lamps could be driven by a square-wave-modulated 250-V dc supply, allowing intermittent photolysis of the reaction mixtures. HO<sub>2</sub> was detected by UV absorption spectroscopy, and was monitored at 220 nm ( $\sigma(HO_2) = 3.40 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ at 220 nm<sup>27</sup>). The behavior of iodine atoms was determined from the observation of the removal and regeneration of  $I_2$  during modulated photolysis, with  $I_2$  detected in absorption at 500 nm. The modulated absorption signals due to  $HO_2$  or changes in  $I_2$ concentration (typically smaller than 10<sup>-3</sup>) were accumulated and averaged in the manner described before.<sup>11</sup>

Flowing gas mixtures were employed for kinetics experiments, so that the buildup of products and complications due to secondary chemistry were minimized. The flows of the constituent gases were either regulated by mass flow controllers (MKS, type 261), or measured with precalibrated rotameters. The concentrations of most of the component gases were determined from the flow rates and measurement of the total pressure in the reaction vessel (MKS, Baratron).  $Cl_2$  and  $I_2$  were measured by conventional absorption spectroscopy at 330 and 500 nm, respectively ( $\sigma$ (330 nm) =  $2.56 \times 10^{-19}$  cm<sup>2</sup> molecule<sup>-1</sup> for Cl<sub>2</sub><sup>28</sup> and  $\sigma(500$  nm) =  $2.19 \times 10^{-18}$  cm<sup>2</sup> molecule<sup>-1</sup> for I<sub>2</sub><sup>29</sup>). A flow of I<sub>2</sub> was achieved by passing a proportion of the gas flow over iodine crystals contained in a sintered glass tube. The tube was either immersed in an ice/water bath or held at room temperature (296 K).  $CH_3OH$  was introduced in a similar manner, by diverting  $N_2$ through a jacketed bubbler containing the liquid. The temperature of the bubbler could be varied to adjust the CH<sub>3</sub>OH vapor pressure.  $Cl_2$  (BOC; 5% in high purity N<sub>2</sub>), H<sub>2</sub> (Air Products; high purity), O<sub>2</sub> (BOC; breathing grade), N<sub>2</sub> (Air Products; high purity), I<sub>2</sub> (BDH; Analar grade), and CH<sub>3</sub>OH (Fisons; AR grade) were used as received. A sample of ICI (BDH; GPR grade, >98%) was further purified by several freeze-pump-thaw cycles, for the purpose of obtaining a reference spectrum.

#### 3. Results

3.1. Discharge-Flow Experiments. The reaction of iodine atoms with HO<sub>2</sub> radicals was studied under pseudo-first-order conditions with as large as possible excess of iodine atoms over HO<sub>2</sub>. Consequently, the rate constant  $k_7$  was derived from the expression:

$$-d \ln [HO_2]/dt = k_7[I]$$
 (i)

The absolute concentrations of iodine atoms were measured before and after each experiment at one of the EPR lines, which was calibrated against O<sub>2</sub>, following the procedure described by Westenberg.<sup>30</sup> Iodine atoms were also titrated against Cl atoms through the conversion reaction

$$CI + ICI \rightarrow I + Cl_2 \tag{16}$$

with ICl in excess over chlorine atoms for which the EPR signal was calibrated previously. The two calibrations were found to give the same result.

The indirect monitoring of HO<sub>2</sub> by OH was shown to be valid from computer simulations of the secondary chemistry occurring in the HO<sub>2</sub>/OH conversion zone. The [HO<sub>2</sub>]/[OH] ratio was found to be effectively independent of the HO<sub>2</sub> concentration at the NO introduction position, for the different concentrations used

TABLE I: Rate Constants for the Reaction I +  $HO_2 \rightarrow HI + O_2$  as a Function of Iodine Atom Concentration (Discharge-Flow Experiments, T = 298 K)

	,			
[1]0ª	k <sub>7</sub> <sup>b</sup>	[I] <sub>0</sub> <sup>a</sup>	$k_{\gamma}^{b}$	
0.53	3.6°	1.27	2.0	
0.69	3.9	1.29	4.6	
0.88	4.3°	1.62	1.50	
0.94	2.9	1.88	1.8	
1.09	4.8	1.92	2.5	
1.11	1. <b>9</b> °	1.99	4.9	
1.17	2.0	2.22	2.3	
	$\bar{k}_7 = (3.1 \pm$	1.2) × 10 <sup>-13</sup>		

<sup>a</sup> Units,  $10^{14}$  molecules cm<sup>-3</sup>. <sup>b</sup> Units,  $10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>c</sup> Experiments performed with an excess of Cl over ICl.

for the other species that reacted with OH (i.e., CH<sub>3</sub>OH, ICl, or  $C_2H_6$ ).

The following ranges of initial concentrations of the reactants were used:  $[I]_0 = (0.53-2.22) \times 10^{14}$  atoms cm<sup>-3</sup> and  $[HO_2] =$  $(1-3) \times 10^{11}$  molecules cm<sup>-3</sup>. The [I]<sub>0</sub> range is rather narrow, but it could not be extended more. At lower [I]<sub>0</sub>, the reaction rates became too low to be measured precisely, whereas at higher  $[I]_0$ , ICl (excess of ICl over Cl) or  $C_2H_6$  (excess of Cl over ICl) reacted too quickly with OH in the conversion zone, due to the large concentrations required.

The pseudo-first-order data obtained from expression i are reported in Table I. The rate constant derived from 14 experiments at 298 K is

 $k_7 = (3.1 \pm 1.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 

The error represents 1 standard deviation to which a further 10% of  $k_7$  has been added to allow for uncertainties in flow and pressure measurements. The error due to the wall recombination of both iodine atoms and HO<sub>2</sub> was found to be negligible, from separate measurements of their recombination rates.

3.2. Molecular-Modulation Experiments. 3.2.1. Photolysis of  $I_2$  in the Presence of  $N_2$  and  $O_2$ : Determination of the Kinetics of Recombination of Iodine Atoms at 298 K and in the Pressure Range 140-760 Torr. Preliminary experiments were performed to investigate the removal and regeneration of I<sub>2</sub> during modulated visible photolysis, with I<sub>2</sub> monitored at 500 nm. The purpose of these experiments was to ensure that changes in  $I_2$  concentration could be used to determine iodine atom concentrations generated in the reaction vessel. Measurements were made at 760-, 250-, 140-, and 50-Torr total pressure of either  $N_2$  or  $O_2$  and with  $I_2$  concentrations of ca.  $10^{15}$  molecules  $\mbox{cm}^{-3}$  . Analysis of the time-resolved absorption wave forms indicated that I2 was regenerated by a second-order process over the pressure range 140-760 Torr (see ref 31 for a detailed account of wave-form analysis). This was due to the recombination reaction of iodine atoms:

$$I + I + M \rightarrow I_2 + M \tag{17}$$

Analysis of the data obtained at 50 Torr indicated a distinct departure from second-order kinetics, which was probably due to the existence of an additional first-order wall recombination route becoming competitive at lower pressures. The values of the observed second-order rate constants, which are attributed to reaction 17, are displayed in Table II. At each pressure, rate constants measured in O2 were approximately a factor of 2 higher than those measured in  $N_2$ , suggesting that  $O_2$  is a more efficient third body. The rate constants displayed a linear dependence on pressure, and the following values of  $k_{17}$  are concluded (T = 298) K):

 $k_{17} = (1.00 \pm 0.05) \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  $(M = N_2)$ 

 $k_{17} = (1.90 \pm 0.10) \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  $(M = O_2)$ 

These values are in good agreement with previously reported rate constants for iodine atom recombination at room temperature in

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ρ/Torr	[N <sub>2</sub> ]/%	[O <sub>2</sub> ]/%	k <sub>17</sub> [M] <sup>a</sup>
135	100		0.45
138		100	0.85
251	100		0.90
252		100	1.75
	100		2.45
	98.5	1.5	3.24
	95	5	4.03
	93	7	4.22
760	87	13	4.20
	80	20	3.92
	63	37	4.52
	21	79	5.09

100

4.85

TABLE II: Values of  $k_{17}$  Determined at Various Pressures of N<sub>2</sub> and/or O<sub>2</sub> (T = 298 K)

<sup>a</sup> Units,  $10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.



Figure 2. Variation of  $k_{17}$  as a function of bath gas composition at atmospheric pressure and 298 K.

the presence of N<sub>2</sub> (1.2 ×  $10^{-32}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> <sup>32</sup>) and O<sub>2</sub> (2.0 ×  $10^{-32}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> <sup>33</sup>).

At 760 Torr, the dependence of  $k_{17}$  on bath gas composition was investigated and was found to be nonlinear as shown in Figure 2. The presence of only small amounts of  $O_2$  (<5%) caused a significant increase in the observed value of  $k_{17}$ . As the  $O_2$ component was increased above 5%,  $k_{17}$  displayed a weaker, apparently linear dependence on composition. The observed rate enhancement in the presence of  $O_2$  cannot be explained in terms of a straightforward efficiency effect or a simple "chaperone" mechanism, since a linear dependence on composition would be expected. Complications in the kinetics of iodine atom recombination in the presence of  $O_2$  have been observed in the past by other authors.<sup>33,34</sup>

3.2.2. Association Reaction of HO<sub>2</sub> Radicals in the Presence of High Concentrations of CH<sub>3</sub>OH at 50 Torr and in the Temperature Range 283-353 K. HO<sub>2</sub> radicals were generated by reaction sequence 13 and 14, initiated by the near-UV-modulated photolysis of Cl<sub>2</sub>. During the experiments to investigate the reaction of iodine atoms with HO<sub>2</sub> (see next section), the reaction of Cl atoms with I<sub>2</sub> occurs in competition with reaction 13, so high concentrations of CH<sub>3</sub>OH were employed (ca. 10<sup>17</sup> molecules cm<sup>-3</sup>) to minimize the complication. Second-order analysis of HO<sub>2</sub> wave forms recorded at 220 nm indicated that CH<sub>3</sub>OH at this concentration had a significant effect on the HO<sub>2</sub> self-reaction rate constant, k<sub>18</sub>, at all temperatures studied (283, 298, 328, and 353 K) and that the effect was greater at lower temperature.

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{18}$$

A similar but weaker dependence of  $k_{18}$  on [CH<sub>3</sub>OH] at 760 Torr has been observed previously.<sup>35</sup> Values of  $k_{18}$  obtained at different

TABLE III: Measured Values of  $k_{18}$  as a Function of [CH<sub>3</sub>OH] and Temperature ( $\rho = 50$  Torr)

T/K	[CH <sub>3</sub> OH] <sup>a</sup>	[N <sub>2</sub> ] <sup>b</sup>	[O <sub>2</sub> ] <sup>b</sup>	k <sub>18</sub> <sup>c</sup>	
283	1.32	12.6	3.2	6.6	
	0	13.6	3.4	1.9 <sup>d</sup>	
298	1.25	12.0	3.0	4.3	
	0.79	12.3	3.1	3.5	
	0.44	12.6	3.2	2.9	
	0	13.0	3.2	1.74	
328	1.14	10.9	2.7	2.3	
	0	11.8	2.9	1.4 <sup>d</sup>	
353	1.06	10.1	2.5	2.1	
	0	10.9	2.7	1.2 <sup>d</sup>	

<sup>a</sup> Units,  $10^{17}$  molecules cm<sup>-3</sup>. <sup>b</sup> Units,  $10^{17}$  molecules cm<sup>-3</sup>. <sup>c</sup> Units,  $10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>d</sup> Values of  $k_{18}$  corresponding to zero [CH<sub>3</sub>-OH] are taken from ref 40 and are included for comparison.

temperatures and [CH<sub>3</sub>OH] are summarized in Table III.

The presence of  $I_2$  in the reaction mixture at concentrations up to ca.  $5 \times 10^{15}$  molecules cm<sup>-3</sup> had no effect on the measured value of  $k_{18}$  at any of the temperatures studied. It was apparent, however, that the production rate of HO<sub>2</sub> was reduced by the presence of  $I_2$  owing to the competing reaction for Cl atoms:

$$Cl + I_2 \rightarrow ICl + I$$
 (19)

Under some conditions, ca. 20% of Cl atoms were scavenged by reaction with  $l_2$ , suggesting that the rate constant for reaction 19 was  $(1-2) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Iodine atoms produced by reaction 19 had no observable effect on HO<sub>2</sub> behavior, giving an indication that the reaction of iodine atoms with HO<sub>2</sub> is slow.

3.2.3. Photolysis of  $Cl_2/CH_3OH/I_2/O_2/N_2$  Mixtures: The Reaction of Iodine Atoms with HO2 at 50 Torr and in the Temperature Range 283-353 K. The aim of these experiments was to investigate the effect of a constant excess concentration of iodine atoms on the behavior of HO2. HO2 was produced by the "modulated" near-UV photolysis of Cl<sub>2</sub>, and simultaneous photolysis of the mixtures with the fluorescent gold lamps allowed production of iodine atoms by the photolysis of  $I_2$  (reaction 15). The photolysis of  $I_2$  was "continuous" in order to achieve the desired constant excess concentration of iodine atoms so that the iodine atom/HO<sub>2</sub> radical reaction would be apparent as a pseudo-first-order contribution to the HO<sub>2</sub> removal, occurring in competition with the  $HO_2$  self-reaction (18). Pairs of experiments were performed in which HO<sub>2</sub> wave forms were recorded with and without I2 photolysis. The concentration of iodine atoms was determined for each set of experimental conditions from an additional experiment during which  $I_2$  was photolyzed intermittently and the removal and regeneration observed at 500 nm, in a similar manner to that described in section 3.2.1. The results of these experiments showed that the behavior of HO<sub>2</sub> was perturbed when  $I_2$  was photolyzed, partially due to the reaction of iodine atoms with HO<sub>2</sub>. Certain complications were apparent, however, precluding a simple description of the reaction system:

(i) Modulated wave forms obtained for the removal and regeneration of  $I_2$ , although displaying rapid changes due to the production and recombination of iodine atoms, also indicated that some  $I_2$  was not regenerated but lost in a stable form (see Figure 3). This was only observed if  $Cl_2$  was present in the system.

(ii) Additional experiments performed during which  $I_2$  was photolyzed with gold lamps (500 <  $\lambda$ /nm < 700) in the presence of Cl<sub>2</sub>, CH<sub>3</sub>OH, O<sub>2</sub>, and N<sub>2</sub> indicated that HO<sub>2</sub> was produced. Once again, Cl<sub>2</sub> had to be present for the production of HO<sub>2</sub> to be observed.

These observations suggest that the photolysis of  $I_2$  in the presence of  $Cl_2$  leads to the production of a stable iodine-containing molecule and Cl atoms that can react to produce HO<sub>2</sub>. One possibility is the reaction of iodine atoms with  $Cl_2$ :

$$I({}^{2}P_{3/2}) + Cl_{2} \rightarrow ICl + Cl$$
 (20)

$$\Delta H^{\circ} = 31.6 \text{ kJ mol}^{-1}$$

Although this reaction is significantly endothermic, there is

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 (34) Strong, J. E.; Prest, H. F.; Strong, R. L. J. Photochem. 1979, 10, 413.

 <sup>(34)</sup> Strong, J. E.; Prest, H. F.; Strong, R. L. J. Photochem. 1979, 10, 413.
 (35) Andersson, B. Y.; Cox, R. A.; Jenkin, M. E. Int. J. Chem. Kinet.
 1988, 20, 283.



Figure 3. Modulated  $I_2$  wave form measured during the photolysis of  $I_2$  in the presence of  $Cl_2$ ,  $CH_3OH$ ,  $O_2$ , and  $N_2$ : (a) rapid changes in absorption due to removal and regeneration of iodine atoms; (b) slower changes in absorption due to production of stable iodine-containing species (ICl), which is removed only by "flow out" from the reaction vessel.

TABLE IV: Experimental Conditions and Fitted Rate Constants For the Reaction  $I + HO_2 \rightarrow HI + O_2$  (Molecular-Modulation Experiments)

-							
T/K	[Cl <sub>2</sub> ]ª	[CH <sub>3</sub> OH] <sup>b</sup>	$[N_2]^b$	[O <sub>2</sub> ] <sup>b</sup>	[I <sub>2</sub> ] <sup>a</sup>	k <sub>7</sub> °	
283	3.9	1.32	12.6	3.2	1.05	$3.95 (\pm 0.7)^d$	_
298	2.2	1.25	12.0	3.0	1.00	$4.7 (\pm 1.5)$ $4.17 (\pm 0.4)^{d}$	
						4.9 (±1.0)	
328	4.5	1.14	10.9	2.7	0.91	6.30 (±0.6)" 7.6 (±1.2)	
353	4.3	1.06	10.1	2.5	0.84	$8.17 (\pm 0.8)^d$	

<sup>*a*</sup> Units,  $10^{15}$  molecules cm<sup>-3</sup>. <sup>*b*</sup> Units,  $10^{17}$  molecules cm<sup>-3</sup>. <sup>*c*</sup> Units,  $10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>*d*</sup> Rate constant determined from analysis of decay curve only.

sufficient energy at the photolysis wavelengths for a process of the following general type to occur:

$$I_{2} + Cl_{2} \xrightarrow{h\nu (500 < \lambda/nm < 660)} ICl + I + Cl \qquad (21)$$
  
$$\lambda = 660 \text{ nm}, \quad \Delta H^{\circ} = 0$$
  
$$\lambda = 500 \text{ nm}, \quad \Delta H^{\circ} = -58.9 \text{ kJ mol}^{-1}$$

This would have to involve either  $I_2$  in an excited electronic state or ground-state  $I({}^2P_{3/2})$  atoms with excess translational energy, since  $I({}^2P_{1/2})$  can only be produced by photolysis at wavelengths below 500 nm.

The production of  $HO_2$  from the photolysis of  $I_2$  needs to be considered when interpreting the perturbation of the modulated  $HO_2$  wave forms by the presence of iodine atoms. Concentrations of  $HO_2$  resulting from  $I_2$  photolysis were measured for each set of experimental conditions and were found to be significantly greater at higher temperatures. The modulated HO<sub>2</sub> wave forms recorded with and without  $I_2$  photolysis were simulated by the FACSIMILE program.<sup>36</sup> A constant (i.e., nonmodulated) HO<sub>2</sub> production route was included to account for HO<sub>2</sub> generated following reaction 21. Initially, the decay curves alone were analyzed, and it was necessary to include the reaction of HO<sub>2</sub> with iodine atoms to obtain good fits to the profiles. The value of  $k_7$ was optimized to obtain the best fit to the data, and the results for each set of experimental conditions are shown in Table IV. Further analyses were performed to simulate the complete modulated wave forms. Experiments performed at 283, 298, and 328 K were well described by the chemical model. A typical pair



Figure 4. Modulated HO<sub>2</sub> wave forms recorded during photolysis of  $Cl_2$  in the presence of CH<sub>3</sub>OH, I<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub>: ( $\bullet$ ) without simultaneous photolysis of I<sub>2</sub>; (O) with photolysis of I<sub>2</sub>; (--) best fit to data with chemical model.



Figure 5. Measured spectra of ICI: continuous line, this work; points, Seery and Britton (ref 28).

of modulated wave forms is shown in Figure 4. The values of  $k_7$  concluded from these analyses were all slightly higher than those obtained from analyzing the decay curves alone (see Table IV) but displayed the same dependence on temperature. At 353 K,  $k_7$  could not be determined from analysis of the complete wave forms since the modulated  $HO_2$  signals observed were greater than those predicted by the model, even if reaction 7 was excluded. This suggests that an additional, unforeseen modulated source of HO<sub>2</sub> was important at 353 K. Further experiments performed at 298, 328, and 353 K with much higher  $I_2$  concentrations displayed a similar complication in the attempted determination of  $k_7$ . At high [I<sub>2</sub>] and temperatures, the production of ICl is favored owing to reactions 19 and 21, allowing accumulation of relatively large amounts in the flow system. Supplementary experiments were performed on static gas mixtures using a diode array camera to record product spectra over the wavelength range 210-690 nm. Figure 5 shows the spectrum obtained for a purified sample of ICl. The cross section at the visible maximum (467 nm) was determined to be  $(4.2 \pm 0.2) \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$  in good agreement with the value reported by Seery and Britton<sup>28</sup> ( $\sigma$ (ca. 470 nm) =  $4.25 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ ). The higher absorptions seen by Seery and Britton in the 290-360-nm region are almost certainly due to Cl<sub>2</sub> impurity, which was subtracted in our spectral analysis. The production of significant amounts of ICl during the photolysis of  $Cl_2/CH_3OH/I_2/O_2$  mixtures was consequently confirmed by comparison of the product spectra with the reference. It is clear from the spectrum of ICl that its photolysis is possible with either the gold lamps or the near-UV black lights with the production of Cl atoms and, subsequently,  $HO_2$  radicals. This

<sup>(36)</sup> Chance, E. M.; Curtis, A. R.; Jones, I. P.; Kirty, C. R. U.K. At. Energy Res. Establ. [Rep.], AERE-R-8775, HMSO: London, 1977.



**Figure 6.** Arrhenius plot of measured values of  $k_7$ : ( $\blacktriangle$ ) discharge flow; ( $\bigcirc$ ) molecular modulation (decay-curve analysis); ( $\bigcirc$ ) molecular modulation (complete wave-form analysis).

is almost certainly the additional modulated source of  $HO_2$  observed in the experiments performed at higher temperature and  $[I_2]$ .

An Arrhenius plot of all rate constants measured in this work is displayed in Figure 6. In view of the complexity of the reaction system during black-light illumination, the analysis of the decay curves is regarded as more reliable. These data lead to the following temperature-dependence expression for the reaction of iodine atoms with HO<sub>2</sub> radicals (error =  $\pm 1\sigma$ ):

$$k_7 = (1.76 \pm 0.75) \times 10^{-11} \exp((-1090 \pm 130)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

At 298 K, this expression leads to a value of  $4.5 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, in reasonable agreement with the value measured by the discharge-flow technique.

#### 4. Discussion

The present discharge-flow and modulated-photolysis determinations of  $k_7$  are the first available data for this reaction. The values measured at 298 K agree well considering the combined uncertainty in the determinations. We recommend the following temperature-dependent expression for  $k_7$ , based on the mean of the discharge-flow and modulated-photolysis determinations at 298 K (3.8 × 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) and the E/R value measured in the modulated photolysis experiments.

$$k_7 = (1.47 \pm 0.63) \times 10^{-11} \exp((-1090 \pm 130)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

These experiments provide additional data for the reactions of  $HO_2$  with atoms and radicals in general. The reactions in this category that have already been studied are those with H, N, O, F, Cl, Br, OH, and HO<sub>2</sub>, and these have been reviewed recently.<sup>18</sup> In addition, the reaction of  $HO_2$  with NO<sub>3</sub> has been investigated recently and independently by the present authors.<sup>37,38</sup> An examination of the reactivity trends for all these reactions is probably not very pertinent, since it is recognized that they do not all proceed by the same mechanism. The mechanisms considered are either a direct H atom transfer from  $HO_2$  or an elimination from a long-lived intermediate.

It is, however, interesting to compare the trend of reactivities of the reactions of  $HO_2$  with the halogen atoms, since now kinetic data are available for the complete series. These data are presented

TABLE V: Kinetic and Thermochemical Parameters for the Reactions of HO<sub>2</sub> with Halogen Atoms

reaction	$\Delta H^a$	k(298 K) <sup>b</sup>	Ab	E/R	ref
$F + HO_2 \rightarrow HF + O_2$	-87	~5			13, 14
-→ OH + FÔ	+13.3				
$CI + HO_{2} \rightarrow HCI + O_{2}$	-54	3.2	1.8	$-170 \pm 200$	15
→ OH + CIO	+1	0.91			
$Br + HO_2 \rightarrow HBr + O_2$	-39	0.2	1.5	$600 \pm 140$	16
-+ OH + BrO	+10.8				
$I + HO_2 \rightarrow HI + O_2$	-22.2	0.038	1.47	1090 ± 130	this work
-→ OH + IO	+21.9				

"Units, kcal mol<sup>-1</sup>. "Units, 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.



Figure 7. Percentage flux through the three major sinks (rural continental troposphere): (a) as a function of  $[CH_3I]$  ( $[O_3] = 40$  ppb); (b) as a function of  $[O_3]$  ( $[CH_3I] = 2$  ppt).

in Table V. The data for the reactions of F, Cl, and Br are taken from ref 13 and 14, 15, and 16, respectively. A recent discharge-flow determination of the room-temperature rate constant for the reaction of Br atoms with HO<sub>2</sub> ( $k = (1.5 \pm 0.2) \times 10^{-12}$ cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-139</sup>) is in good agreement with the value of Toohey et al.<sup>16</sup> A comparison of reactivities can be made for the channel X + HO<sub>2</sub>  $\rightarrow$  HX + O<sub>2</sub> (X = F, Cl, Br, I) since, except for Cl, it is the only significant channel at ambient temperatures, the alternative channel (producing XO and OH) having too high an endothermicity. It can be seen from Table V that the reactivity at 298 K decreases from X = F to I. This decrease can be correlated with the exothermicity. The *A* factors are comparable (ca. (1.5-5)  $\times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) and indicate a direct H atom transfer mechanism as recently discussed.<sup>18</sup> Consequently, the values of *E/R* increase from X = F to I.

#### 5. Atmospheric Chemistry

The reaction between iodine atoms and  $HO_2$  radicals is a potential "sink" or "storage" reaction for iodine in the lower atmosphere that, along with the other sink reactions (4-6), may influence the concentrations of iodine atoms and IO radicals, as indicated in the Introduction. The relative importance of the

<sup>(37)</sup> Mellouki, A.; Le Bras, G.; Poulet, G. J. Phys. Chem. 1988, 92, 2229.
(38) Hall, I. W.; Wayne, R. P.; Cox, R. A.; Jenkin, M. E.; Hayman, G. D. J. Phys. Chem. 1988, 92, 5049.

<sup>(39)</sup> Laverdet, G.; Le Bras, G.; Mellouki, A.; Poulet, G. To be published.

TABLE VI: Kinetic Parameters and Ambient Concentrations of Trace Species Used in Atmospheric Model

reaction	rate or equilib const	ref
$CH_{3}I + h\nu \rightarrow CH_{3} + I$ $I + O_{3} \rightarrow IO + O_{2}$ $I + HO_{2} \rightarrow HI + O_{2}$ $I + NO = INO$ $I + NO_{2} \Rightarrow INO_{2}$ $IO + NO \rightarrow I + NO_{2}$ $IO + h\nu \rightarrow I + O$	$3.0 \times 10^{-6a}$ 9.5 × 10 <sup>-13b</sup> 3.8 × 10 <sup>-13</sup> 10 <sup>-5.7</sup> exp(9160/T) <sup>c</sup> 10 <sup>-6.4</sup> exp(9560/T) 1.7 × 10 <sup>-11</sup> 3.0 × 10 <sup>-2</sup>	1 40 this work 45 45 40 40
$IO + DMS \rightarrow I + DMSO$ $IO + NO_2 \stackrel{M}{\longrightarrow} IONO_2$ $IO + IO \rightarrow I_2O_2$ $IO + IO \rightarrow 2I + O_2$ $IO + HO_2 \rightarrow HOI + O_2$ $HI + OH \rightarrow H_2O + I$ $IONO_2 + h\nu \rightarrow I + NO_3$	$2.0 \times 10^{-11}$ $2.7 \times 10^{-12}$ $5.2 \times 10^{-11}$ $1.0 \times 10^{-11}$ $4.0 \times 10^{-12}$ $3.3 \times 10^{-11}$ $6.4 \times 10^{-3}$	8, 9 11 40 2 1 39 1
$IONO_2 \stackrel{M}{\longrightarrow} IO + NO_2$ $HOI + h\nu \rightarrow OH + I$ $I_2O_2 + h\nu \rightarrow 2I + O_2$ $I_2O_2 \rightarrow I_2O_2(ads)$ $I_2O_2(ads) \rightarrow I_2O_2$ $IONO_2 \text{ deposition}$ HI  deposition $I_2O_2(ads) \text{ deposition}$	$5.0 \times 10^{-3} \\ 6.3 \times 10^{-3} \\ 3.0 \times 10^{-5} \\ 2.5 \times 10^{-3d} \\ 5.0 \times 10^{-4e} \\ 1.8 \times 10^{-5} \\ 1.0 \times 10^{-5} \\ 2.0 \times 10^{-5} \\ 2.0 \times 10^{-5} \\ 2.0 \times 10^{-6} \end{cases}$	2 1 see text see text 2 2 2

[CH<sub>3</sub>I] varied in the range  $5.0 \times 10^{6} - 5.0 \times 10^{8}$  molecules cm<sup>-3</sup> varied in the range  $5.0 \times 10^{10}$ - $2.5 \times 10^{12}$  molecules cm<sup>-3</sup> [O<sub>3</sub>]  $1.25 \times 10^{10d}$  or  $3.0 \times 10^9$  molecules cm<sup>-3e</sup> [NO]  $5.0 \times 10^{10d}$  or  $1.0 \times 10^{10}$  molecules cm<sup>-3e</sup>  $[NO_2]$  $1.1 \times 10^6$  molecules cm<sup>-3 f</sup> IOH  $2.1 \times 10^8$  molecules cm<sup>-3 f</sup>  $[HO_2]$ zero<sup>d</sup> or  $3.0 \times 10^9$  molecules cm<sup>-3e</sup> [DMS] 1000 cm<sup>-3d</sup> or 200 cm<sup>-3e</sup> particle

density

<sup>a</sup>Units are s<sup>-1</sup> for unimolecular reactions. <sup>b</sup>Units are cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for bimolecular reactions. Rate constants for pressure-dependent reactions calculated for a gas density of  $2.5 \times 10^{19}$  molecules cm<sup>-3</sup>. <sup>c</sup>Units are atm<sup>-1</sup> for equilibrium constants. <sup>d</sup>Rural continental air mass. <sup>e</sup>Marine coastal troposphere. <sup>f</sup>Steady-state values generated in 2D tropospheric model<sup>47</sup> corresponding to latitude 45° N.

production of IONO<sub>2</sub> (reaction 4),  $I_2O_2$  (reaction 5), and HI (reaction 7) as sinks for atmospheric iodine has been calculated previously for a rural continental air mass.<sup>2</sup> These calculations suggested that HI formation via reaction 7 was a significant removal process for iodine, particularly at low O<sub>3</sub> concentrations (see Figures 8 and 9 of ref 2). Under these circumstances the ratio [I]/[IO] is enhanced, owing to the reduced rate of reaction 1, and the importance of sink processes involving iodine atoms is increased. Figure 7 shows the results of similar calculations with updated rate constants. The complete model is shown in Table VI. The following rate constant modifications have been made:

(a)  $I + HO_2 \rightarrow HI + O_2$ . The 298 K value of  $3.8 \times 10^{-13} \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> determined in this work is used instead of the previously estimated value of  $5 \times 10^{-13} \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>.<sup>2</sup>

(b)  $OH + HI \rightarrow I + H_2O$ . The rate constant for this reaction has recently been determined to be  $3.3 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1.40</sup> This is, however, very close to the previously estimated value of  $2.5 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1.1</sup>

(c)  $IO + IO \stackrel{\text{M}}{\longrightarrow} I_2O_2$ . A value of  $5.2 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> was used,<sup>41</sup> and this is significantly smaller than that used previously (1.6  $\times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-12</sup>). The photolysis of I<sub>2</sub>O<sub>2</sub> was also included in competition with attachment to atmospheric particulate. The rate of I<sub>2</sub>O<sub>2</sub> photolysis was taken to be 1 order of magnitude faster than for CH<sub>3</sub>I. This is based on the strong featureless product absorption extending to wavelengths above 300 nm observed by Sander.<sup>12</sup> The rate of attachment to

(41) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F.; Kerr, J. A.; Troe, J. J. Phys. Chem. Ref. Data 1989, 18, 881.



Figure 8. Percentage flux through the three major sinks (coastal troposphere): (a) as a function of  $[CH_3I]$  ( $[O_3] = 30$  ppb); (b) as a function of  $[O_3]$  ( $[CH_3I] = 2$  ppt).

the atmospheric aerosol was calculated assuming the mean particle radius to be  $10^{-6}$  m and the accommodation coefficient (sticking probability) to be  $2.5 \times 10^{-3}$ . A residence time of 15 h was assumed for an  $I_2O_2$  molecule on the surface of a particle before desorption. These figures are based on those measured for  $I_2$  by Garland.<sup>42</sup>

Figure 7 indicates that, even with these modifications, the picture is much the same as calculated before. The importance of both iodine oxide and HI deposition is reduced, with the flux through the  $IONO_2$  route remaining approximately unchanged.

The calculations discussed above refer to rural continental air. If we now consider the marine coastal troposphere, where NO<sub>x</sub> levels are significantly lower (see Table VI), then the relative importance of the sink routes is as displayed in Figure 8. Under these conditions, IO concentrations are enhanced relative to iodine atom concentrations (e.g., about 1 order of magnitude greater for  $[O_3] = 30$  ppb), because the conversion route for IO into iodine atoms by reaction with NO is considerably reduced. As a consequence, sink routes involving IO radical reactions are favored compared with the high NO<sub>x</sub> scenario, in particular the formation of  $I_2O_2$ , since the rate of its formation is proportional to  $[IO]^2$ and does not involve  $NO_x$ . The production of  $IONO_2$  is not as important as at high NO<sub>x</sub> owing to the reduced NO<sub>2</sub> concentration. It is possible that the formation of HOI via reaction 6 may become significant as an iodine sink at low NO<sub>x</sub>, but this was not considered specifically in these calculations. The formation of HI via reaction 7 is significant but remains the minor sink unless O<sub>3</sub> concentrations are low.  $O_3$  concentrations in oceanic air do not typically fall below ca. 10 ppb, however.

Concentrations of IO generated by the model were in excess of 10<sup>6</sup> molecules cm<sup>-3</sup> for  $[CH_3I] = 2$  ppt and  $[O_3] = 30$  ppb, with the low-NO<sub>x</sub> scenario. This suggests that the atmospheric lifetime of DMS before reaction with IO is ca. 10 h, based on currently published rate constants for reaction 2 (k(IO + DMS))

<sup>(40)</sup> Mellouki, A. Ph.D. Thesis, Orléans, France, 1989.

<sup>(42)</sup> Garland, J. A. J. Nucl. Energy 1967, 21, 687.

=  $2 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-18,9</sup>). This should be compared with the lifetimes before reaction with OH and NO<sub>3</sub>, which are both ca. 30 h ([OH]  $\simeq 10^6$  molecules cm<sup>-3</sup>,  $k(OH + DMS) = 8 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>;<sup>43</sup> [NO<sub>3</sub>]  $\simeq 10^7$  molecules cm<sup>-3</sup>,  $k(NO_3 + DMS) = 9 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>4<sup>4</sup>). This suggests that IO may be a potentially important oxidizing radical in the marine boundary layer. The impact of halogen oxides on DMS oxidation has been discussed recently by Barnes et al.45

(44) Mean value of the literature determinations reported in: Dlugokencky, E. J.; Howard, C. J. J. Phys. Chem. 1988, 92, 1188. (45) Barnes, I.; Becker, K. H.; Martin, D.; Carlier, P.; Mouvier, G.;

Jourdain, J. L.; Laverdet, G.; Le Bras, G. In *Biogenic Sulphur in the Envi-ronment*; Saltzman, E. S., Cooper, W. J., Eds.; ACS Symposium Series No. 393; American Chemical Society: Washington, DC, 1989; p 464. (46) Van den Bergh, H.; Troe, J. J. Chem. Phys. 1976, 64, 736.

(47) Derwent, R. G.; Curtis, A. R. U.K. At. Energy Res. Establ., [Rep.], AERE-R-8853; HMSO: London, 1977.

Although there as been some progress in recent years in measuring rate constants for iodine reactions of potential atmospheric importance, there are still many uncertainties, and it is possible that the above conclusions may be changed dramatically as key parameters are determined. It appears, however, that sink routes involving reactions of IO are likely to be important. In this respect, the reaction of IO with HO<sub>2</sub> needs to be studied in addition to confirmation of the single measurement of the IO + NO<sub>2</sub> reaction.<sup>11</sup> Detection of the products HOI, IONO<sub>2</sub>, and I<sub>2</sub>O<sub>2</sub> is also of great importance, together with measurement of their thermal decomposition rates and characterization of their UVvisible absorption spectra to assist in determining their atmospheric lifetimes before photolysis.

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# Krypton Chloride and Krypton Fluoride Thermochemistry and Formation and Relaxation Kinetics in Ar, N<sub>2</sub>, and CF<sub>4</sub> Buffer Gas

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Krypton chloride and krypton fluoride molecules were formed by the  $Kr({}^{3}P_{1})$  sensitization reaction with  $Cl_{2}$  or  $F_{2}$  in variable pressures (up to 5 atm) of Ar, N<sub>2</sub>, and CF<sub>4</sub> buffer gases at 300 and 230 K. Less extensive experiments also were done in He and Ne. The high-pressure (equilibrium) KrF(C)/KrF(B) and KrCl(C)/KrCl(B) ratios were observed in order to assign the energy separation of the C and B states. Although not totally conclusive, the present data support  $\Delta E_{BC}$  (= $E_{C} - E_{B}$ ) values of  $-120 \pm 50$  and  $0 \pm 50$  cm<sup>-1</sup> for KrF\* and KrCl\*, respectively. The KrF(B,C) + 2Ar rate constant for ArKrF\* formation was assigned as (8 ± 3) × 10<sup>-33</sup> cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> at 300 K; a slightly larger value was estimated for formation of ArKrCl\*. Three-body formation of ArKrF\* and ArKrCl\* in Ar buffer was enhanced by reduction of the temperature. The increase in KrF(D) and KrCl(D) concentration, relative to KrF(B,C) and KrCl(B,C), with increased Ar pressure is attributed to the larger three-body quenching rates for the KrF(B,C) and KrCl(B,C) states. The C  $\rightarrow$  B collisional transfer and the vibrational relaxation of KrF(B,C) and KrCl(B,C) also are discussed.

### I. Introduction

The  $Kr({}^{3}P_{1})$  sensitization technique with  $Kr/X_{2}$  (X = F, Cl) mixtures with added buffer gas provides a steady-state method for studying the relaxation and quenching of KrF(B,C) and KrCl(B,C) molecules from the low-pressure, collision-free limit up to  $\sim 5$  atm pressure.<sup>1-5</sup> Early work<sup>1,4</sup> at low pressure established that  $Xe({}^{3}P_{1})$  and  $Xe({}^{3}P_{2})$  or  $Kr({}^{3}P_{1})$  and  $Kr({}^{3}P_{2})$  reacted in similar ways with halogen-containing reagents with respect to product branching fractions and vibrational energy disposal. In the present study the work is extended to high buffer gas pressure for KrF\* and KrCl\* at 300 and 230 K with the main objective of measuring the B- and C-state energy separations. Since the ArKrF\* and ArKrCl\* emission spectra<sup>1b</sup> overlap the KrF(C-A) and KrCl(C-A) bands, experiments were done in  $N_2$  and CF<sub>4</sub> to circumvent trimer formation. The variation of the  $I_{ArKrX}/I_{KrX(B,C)}$  ratio with Ar pressure was used to assign the ArKrX\* formation rate constants. The three-body quenching of the B and C states seems to be more rapid than that of the D state, leading to an apparent increase in the steady-state KrF(D) and KrCl(D) populations for high pressure of Ar. In addition to interpretation of the high-pressure data for KrF\* and KrCl\* and discussion of the formation rates of ArKrF\* and ArKrCl\*, some low-pressure spectra are shown to demonstrate that the general pattern for

vibrational relaxation and  $C \rightarrow B$  transfer for KrF\* and KrCl\* closely resembled the extensively documented XeCl\* case.<sup>2</sup> Kvaran, Shaw, and Simons<sup>5</sup> have used the sensitization technique to model the vibrational relaxation of KrF(B). In previous work using the  $Kr({}^{3}P_{1})$  and  $Xe({}^{3}P_{1})$  sensitization technique, we have identified some mixed rare gas halide trimer spectra,<sup>1b</sup> studied the C-B transfer and vibrational relaxation of XeCl in high vlevels,<sup>2</sup> assigned values of the B-C-state energy separation for xenon halides, and made some refinements to the xenon halide C(3/2) and A(3/2) potential curves.<sup>3</sup>

In contrast with the xenon halides, the energy separation between the B and C states of KrX\* has not been assigned with confidence. Tellinghuisen and McKeever<sup>6</sup> used their high-pressure (≤750 Torr of Ar) Tesla coil discharge technique to study KrCl\*, and they recommended  $\Delta E_{BC} = E_C - E_B = 375 \pm 70 \text{ cm}^{-1}$  with

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