excited ground electronic state of Br<sub>2</sub> was made. NeCl<sub>2</sub> remains as the only example of a van der Waals molecule whose metastable states are observed to live more than  $10^{-5}$  s.

Acknowledgment. This work was supported by the National Science Foundation Grant No. CHE-8202408 and by the Atlantic Richfield Corp. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No. Br<sub>2</sub>, 7726-95-6; <sup>81</sup>Br<sub>2</sub>, 30680-77-4; <sup>79</sup>Br<sup>81</sup>Br, 17523-63-6; <sup>79</sup>Br<sub>2</sub>, 29120-28-3; Ne, 7440-01-9.

## Rate and Product Measurements for the Reactions of OH with Cl<sub>2</sub>, Br<sub>2</sub>, and BrCl at 298 K. Trend Interpretations

## Lee M. Loewenstein and James G. Anderson\*

Department of Chemistry and Center for Earth and Planetary Physics, Harvard University, Cambridge, Massachusetts 02138 (Received: May 15, 1984)

The reaction rate constants for OH + Cl<sub>2</sub>, Br<sub>2</sub>, and BrCl are determined to be  $6.70 \times 10^{-14}$ ,  $5.28 \times 10^{-11}$ , and  $1.49 \times 10^{-12}$ cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively. Rate measurements are carried out at 298 K in He by using a discharge flow apparatus. Two OH sources are used:  $H + NO_2$ , and  $F + H_2O$ . OH decays are monitored by resonance fluorescence at 309 nm; Cl and Br are measured simultaneously with OH by resolved resonance fluorescence at 134.7 and 157.7 nm, respectively. Measurement of OH + BrCl requires corrections for  $Cl_2$  and  $Br_2$  which exist in equilibrium with BrCl. Atom yields from the title reactions are compared to the reference reactions  $H + Cl_2$  and  $Br_2$  and analyzed by a computer model of the reaction kinetics. The products in each case are found to be the halogen atoms (Cl and Br), and not the halogen oxide radicals (ClO and BrO). Using the observed, forward reaction rate constants and the equilibrium constants derived from thermodyanmic data, we calculate the rate constants of the reverse reactions, Cl + HOCl, Br + HOBr, and Cl + HOBr, to be 2.5 × 10<sup>-12</sup>,  $2.4 \times 10^{-17}$ , and  $3.7 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively. The reactivity of OH toward the three halogen molecules is related to the ionization potentials of the halogens, lower ionization potentials promoting faster reactions. In addition, a comparison of the results obtained here with the rate constant measurements of other radical-halogen reactions indicates that a radical's reactivity correlates with its electron affinity. On the basis of these trends, the activation energies of the title reactions are estimated to be 2.1, 0.0, and 3.4 kcal mol<sup>-1</sup>, respectively. The dependence of the rate constant on the ionization potential and electron affinity of the reactants may serve as a guide for estimating the rates of similar radical-molecule reactions.

## Introduction

The chemistry of the hydroxyl radical is fairly well characterized in many systems. The OH radical is of such paramount importance in the atmosphere and in flames that many of its reactions with molecules such as CO and CH<sub>4</sub> have received considerably attention. The reactions of OH with halogens and interhalogens have been far less completely determined; only

$$OH + Cl_2 \rightarrow products^{1,2}$$
 (1)

and

$$OH + Br_2 \rightarrow products^3$$
 (2)

have been studied at present. Although these reactions are not directly important to either atmospheric or flame processes, they and similar reactions have the potential of exhibiting diverse behavior through a potential multiplicity of available product channels. Reaction 2 may serve as a useful source<sup>3</sup> for photochemical studies of HOBr, which has been suggested as a participant in several catalytic cycles destroying stratospheric ozone.<sup>4</sup>

For the above reactions, the channels<sup>5</sup>

-----

$$OH + Cl_2 \rightarrow HOCl + Cl \qquad \Delta H = 1.8 \text{ kcal mol}^{-1} \text{ (ref 6)}$$
(1a)

$$OH + Cl_2 \rightarrow HCl + ClO$$
  $\Delta H = -7.3 \text{ kcal mol}^{-1}$  (1b)

 $OH + Br_2 \rightarrow HOBr + Br$  $\Delta H = -9.1 \text{ kcal mol}^{-1} \text{ (ref 7)}$ (2a)

$$OH + Br_2 \rightarrow HBr + BrO$$
  $\Delta H = 4.5 \text{ kcal mol}^{-1} \text{ (ref 7)}$ 
(2b)

are thermodynamically accessible at room temperature, although channels 1a and 2b must, of course, have activation energies at least equal to the enthalpies of reaction. Of these channels, only reaction 2a has been determined directly.<sup>3</sup> The reaction of OH with BrCl also has numerous reaction pathways available:

$OH + BrCl \rightarrow HOCl + Br$	$\Delta H = -4.7 \text{ kcal mol}^{-1}$	(3a)
$OH + BrCl \rightarrow HOBr + Cl$	$\Delta H = -2.9 \text{ kcal mol}^{-1}$	(3b)

 $OH + BrCl \rightarrow HCl + BrO$  $\Delta H = -5.0 \text{ kcal mol}^{-1}$ (3c)

$$OH + BrCl \rightarrow HBr + ClO$$
  $\Delta H = 2.6 \text{ kcal mol}^{-1}$  (3d)

The formation of HOX + X' (X and X' both being halogens) through channels 1a, 2a, 3a, and 3b—likely proceeds through a linear chain transition state, while the production of HX + X'O-through channels 1b, 2b, 3c, and 3d-would imply passage through a cyclic four-center transition state.

The analogous reactions of  $O(^{3}P)$  with these same halogens have been studied by Clyne and co-workers:<sup>8</sup>

$$O + Cl_2 \rightarrow ClO + Cl \qquad \Delta H = -6.4 \text{ kcal mol}^{-1}$$
 (4)

$$O + Br_2 \rightarrow BrO + Br$$
  $\Delta H = -10.3 \text{ kcal mol}^{-1}$  (5)

 $O + BrCl \rightarrow BrO + Cl$  $\Delta H = -4.2 \text{ kcal mol}^{-1}$  (6)

These reactions have fewer possible product channels than re-

<sup>(1)</sup> Leu, M. T.; Lin, C. L. Geophys. Res. Lett. 1979, 6, 425.

<sup>(2)</sup> Ravishankara, A. R.; Eisele, F. L.; Wine, P. H. J. Chem. Phys. 1983, 78, 1140.

<sup>(3)</sup> Poulet, G.; Laverdet, G.; Le Bras, G. Chem. Phys. Lett. 1983, 94, 129. (4) Yung, Y. L.; Pinto, J. P.; Watson, R. T.; Sander, S. P. J. Atmos. Sci. 1980, 37, 339.

<sup>(5)</sup> Except where indicated, thermochemical quantities are derived from: Stull, D. R., Prophet, H., Eds. "JANAF Thermochemical Tables", 2nd ed.; U.S. Department of Commerce: Washington, DC, 1981; NSRDS-NBS37. (6)  $\Delta H_1$ (HOCl) as determined by Knauth, H. D.; Alberti, H.; Clausen, H.

J. Phys. Chem. 1979, 83, 1604 is used, instead of the value from ref 5.

<sup>(7)</sup>  $\Delta H_f(BrO, HOBr, and HOF)$  are obtained from: Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976. (8) Clyne, M. A. A.; Monkhouse, P. B.; Townsend, L. W. Int. J. Chem.

Kinet. 1976. 8, 425.



Figure 1. Schematic of the discharge flow apparatus. The four major sections—detection chamber, reaction zone, radical source, and dead volume—are joined by O rings. The tube comprising the reaction zone may be replaced by similar ones with different diameters. Radical source A produces OH by means of  $H + NO_2$ ; radical source B (inset) produces OH by the reaction  $F + H_2O$ .

actions 1-3. They also differ in their thermochemistry by an amount equal to that of the reaction  $O + HOX \rightarrow OH + XO$ , and in the electronic nature of the radical reactants. The consequence of these differences on the course of reaction will be considered.

We have studied reactions 1–3 at 298 K, determining the overall reaction rates of OH with  $Cl_2$ ,  $Br_2$ , and BrCl, and the branching ratios for the majority of the channels enumerated above. The techniques used are generally applicable to the study of other OH-halogen reactions: simultaneous measurements of OH and halogens by resolved resonance fluorescence, chemical conversion of halogen oxide radicals to halogen atoms, and calibration of the halogen yields by known reactions coupled with computer simulations of the kinetics. This is is the first report to appear on the chemistry of reaction 3.

## **Experimental Section**

The apparatus couples a discharge flow reaction (Figure 1) for producing radicals and carrying out radical-molecule reactions, with a dual-axis detection chamber (Figure 2) for observing radical reactants and atomic products. The apparatus is new and is described in detail below.

Discharge Flow Reactor. The main reactant manifold includes a 5-L reservoir of Pyrex, in which the gases  $Cl_2$ ,  $Br_2$ , and BrCl are stored, diluted in He. In this manifold, the pressure relative to atmospheric is measured with a reluctance manometer (Validyne, Model DP7). Other manifolds have 0.5-L reservoirs of stainless steel and use Bourdon gauges (Matheson, vacuum-2 atm) for measuring the absolute pressure. Small pressure changes, which occur when preparing a gas mixture and when eluting reactants from the reservoirs, are measured on Validyne gauges used as differential pressure transducers. Stainless steel needle valves control gas flows from the manifolds.

The Pyrex flow tube is coated with halocarbon wax (Halocarbon Products Corp.) in order to minimize the loss of atoms and radicals on the reactor wall. The prepared surface is generally stable over time. The OH wall loss ranges from 2 to 5 s<sup>-1</sup> in a 25 mm i.d. tube at 3 torr, corresponding to a wall recombination coefficient<sup>9</sup> for OH,  $\gamma_{OH}$ , of (3–8) × 10<sup>-5</sup>.  $\gamma_{H}$  is approximately 2 × 10<sup>-5</sup>, while  $\gamma_{C1}$  and  $\gamma_{Br}$  on the halocarbon wax surface are both under 1 × 10<sup>-5</sup>. Three tube i.d.'s—16, 25, and 32 mm—are used to test for surface effects on the rate constants by varying the reactor's surface-to-volume ratio.

Measured upstream from the OH detection axis, the positions of various points are as follows: 7 cm to the edge of the chamber



Figure 2. Detection chamber with dual radical and atom detection axes. The flowing  $H_2O$  vapor lamp is used to measure OH by resonance fluorescence. Cl and Br are measured by using a sealed  $Cl_2$  lamp (not shown) or a flowing Br<sub>2</sub> vapor lamp, respectively; resonance fluorescence is resolved by the vacuum-ultraviolet monochromator. A 2.5 cm i.d. insert lies between the two axes to confine the gas flow.

(a 2.5 cm i.d. halocarbon-coated insert is always used in this section regardless of the i.d. of the rest of the reactor); 10 cm to an NO loop injector, which is used in conversion of ClO to Cl and BrO to Br by the reactions<sup>10</sup>

$$ClO + NO \rightarrow Cl + NO_{2} \qquad k =$$

$$1.6 \times 10^{-11} \text{ cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1} (7)$$

$$BrO + NO \rightarrow Br + NO_{2} \qquad k =$$

$$2.1 \times 10^{-11} \text{ cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1} (8)$$

The flow tube pressure is measured against a vacuum reference with a Validyne pressure transducer 15 cm farther upstream.

The distance (from the OH axis) to the NO<sub>2</sub> addition port is 75 cm, and 80 cm to the point of H atom addition, both part of radical source A in Figure 1. The He carrier gas is added 5 cm farther upstream. H<sub>2</sub> (5-10% in UHP He) is discharged in an uncoated quartz tube to produce H atoms. OH is rapidly formed in an excess of NO<sub>2</sub> (approximately  $10^{12}$  molecules cm<sup>-3</sup>) by<sup>11</sup>

$$H + NO_2 \rightarrow OH + NO$$
  $k =$ 

 $1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (9)

The same discharge tube serves to produce O atoms from an  $O_2$  discharge in several experiments. The rear section of the reactor, extending to 152 cm, serves as a "dead volume" to segregate the forward part of the sliding injector from the air exterior to the reactor.

A different flow tube section (radical source B in Figure 1) replaces the one above when making OH by  $F + H_2O$ . It consists of a 50 cm long, 1 cm i.d., halocarbon-wax-coated side arm which appends the reactor at 80 cm. The He carrier gas is added near the rear of the side arm.  $CF_4$  (10% in He) is discharged to produce F atoms in a tube made of alumina (Coors). The alumina directly abuts the halocarbon-wax-coated side arm, preventing radicals exiting the discharge from contacting the machined stainless steel union.  $H_2O$  is added to the flow through a 3.2 mm o.d. Teflon tube inserted down the center of the side arm. This serves as a second source of OH, produced by the reaction

$$F + H_2O \rightarrow OH + HF$$
  $k =$   
1.1 × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (10)

An excess of  $H_2O$  rapidly converts all F to OH. The CF and CF<sub>3</sub> radicals produced<sup>12</sup> along with F could potentially interfere with

<sup>(9)</sup> Howard, C. J. J. Phys. Chem. 1979, 83, 3.

<sup>(10)</sup> Unless otherwise indicated, rate constants are recommended by: DeMore, W. B.; Watson, R. T.; Golden, D. M.; Hampson, R. F.; Kurylo, M.; Howard, C. J.; Molina, M. J.; Ravishankara, A. R. "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling: Evaluation Number 5"; Jet Propulsion Laboratory: Pasadena, CA, 1982; JPL Publication 82-57. (11) Hampson, R. F. Report FAA-EE-80-17; U.S. Department of

<sup>(11)</sup> Hampson, R. F. Report FAA-EE-80-17; U.S. Department of Transportation: Washington, DC, 1980.

the rate and product measurements carried out. The consistency of the rate constant measurements from the OH source reactions 9 and 10 indicates that the presence of these discharge byproducts does not have any measurable effect on the course of reaction. The agreement of two independent radical sources shows that no systematic error results from the method of preparing OH, as a consequence of the various gases present-NO, NO2 and H2 from the H + NO<sub>2</sub> source, and HF,  $CH_4$ , and  $H_2O$  from the F +  $H_2O$ source. Reaction 10 is used only for rate measurements, and not for product studies.

Electronic mass flowmeters (Matheson) measure the total flow of carrier gas through the reactor. The bulk flow of gas down the tube is set up by a Welch 1397 mechanical pump, separated from the reactor by a 5-L ballast volume. In the 25 mm tube, for instance, flow velocities are commonly near 12 m s<sup>-1</sup>. Velocities are typically varied from 6 to 22 m  $s^{-1}$ .

A 160 cm long, 6.3 mm o.d., Pyrex sliding injector moves along the center of the flow tube, supported on a Teflon tripod. It is coated both internally and externally with halocarbon wax and has a wall loss toward OH of about  $1 \text{ s}^{-1}$ . At its tip is a Teflon plug with eight radially distributed holes. A flexible stainless steel tube connects the reactant reservoir to the injector.

A 14 mm o.d. quartz tube, coated with baked phosphoric acid, lies at the rear of the injector, within a microwave discharge cavity exterior to the flow tube.  $Cl_2$  and  $Br_2$  are discharged in this cavity in experiments to measure the loss of Cl and Br atoms on the reactor wall.

During Cl and Br atom fluorescence calibrations, O<sub>2</sub> and CF<sub>4</sub> in He are discharged as mentioned above, producing O and F atoms, respectively, while the reactants Cl<sub>2</sub> and Br<sub>2</sub> are added to the reactor through the injector. Cl and Br atoms are formed by the reactions

$$F + Cl_2 \rightarrow Cl + ClF$$
  $k =$   
1.6 × 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (ref 13) (11)

$$O + Br_2 \rightarrow Br + BrO$$
  $k =$   
1.4 × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (ref 8) (12)

$$O + BrO \rightarrow Br + O_2$$
  $k = 2.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 
(13)

In an excess of O atoms, reactions 12 and 13 produce two Br atoms for each Br<sub>2</sub> molecule added.

Atom fluorescence calibrations are also carried out by a second method for both Cl and Br. The reactions of Cl2 and Br2 with H atoms14

$$H + Cl_2 \rightarrow Cl + HCl \qquad k = 2.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
(14)

$$H + Br_2 \rightarrow Br + HBr \qquad k = 5.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
(15)

produce halogen atoms quantitatively. The secondary reactions<sup>14</sup>

H + HCl 
$$\rightarrow$$
 Cl + H<sub>2</sub>  $k = 4.4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 

 $H + HBr \rightarrow Br + H_2$  $k = 1.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 

are sufficiently slow as to not cause significant interference. In addition, conversion of H to OH by reaction 9 allows reactions 14 and 15 to serve as reference to halogen atom production from reactions 1-3. By this approach, the temporal formation of products can be followed and compared to the halogen production curves predicted by a computer model.

The discharges used to produce radicals occur in  $1/_4$ -wave microwave cavities, with power provided by magnetrons operating at 2.45 GHz. Radical discharges typically receive 40-50 W.

Resonance Fluorescence Detection System. The OH radical is detected by its  $A^2\Sigma^+$  (v = 0)- $X^2\Pi$  (v = 0) electronic transition at 309 nm. A flowing mixture of  $H_2O$  in He at 1-2 torr is discharged in a quartz lamp, with 70 W of microwave power. Radiation from the lamp is collimated by a series of baffles, painted black to reduce scattered light, before passing through a quartz window into the detection chamber. Two light traps, 5 cm deep, are positioned opposite the lamp and photomultiplier tube ports. Photons scattered at 90° to the incident beam exit the chamber through another quartz window and series of collimating baffles. An interference filter, centered at 309.0 nm with a bandwidth of 5.0 nm, lies immediately before the photomultiplier tube (PMT). Two PMTs (EMR 510N and Hamamatsu R647) are used at different times. Photons are counted with a Hewlett-Packard 5300B pulse counting system; the signal is plotted on a stripchart recorder by way of a digital-analog converter (Hewlett-Packard 5311B).

The OH detection sensitivity is determined by adding NO<sub>2</sub> to an excess of H, according to reaction 9. A typical detection efficiency for OH in this arrangement is  $1 \times 10^{-8}$  count s<sup>-1</sup>/ (molecule  $cm^{-3}$ ), with a scattered signal of about 30 counts  $s^{-1}$ With 10-s integration periods, the minimum detectable [OH] (S/N = 1) is  $2 \times 10^8$  molecules cm<sup>-3</sup>. The sensitivity of the Hamamatsu tube is about half that of the EMR.

The atom detection ports are 6 cm downstream of the OH axis. A 2.50 cm i.d. tube, coated with halocarbon wax, is supported on a Teflon ring between the two axes. One light trap lies opposite the halogen atom lamp port during fluorescence measurements. The lamp may also be positioned opposite the entrance slit of the monochromator for direct observation of the lamp's emission spectrum. The front of the lamp is sealed to the detection chamber by an O ring. A 30 cm focal length, Czerny-Turner monochromator (McPherson 218) with a 3600 line mm<sup>-1</sup> plane grating (Bausch and Lomb) and evacuated with an oil diffusion pump abuts the chamber, separated from it by a MgF<sub>2</sub> window. The PMT (EMR 510G) used with the monochromator has a CsI photocathode.

The chlorine lamp, previously described by Schwab and Anderson,<sup>15</sup> consists of front and rear MgF<sub>2</sub> windows sealed to a quartz body with two side arms. One of these side arms contains  $PtCl_4$  which is resistively heated to release  $Cl_2$ , and the other a Ba getter. The strong  ${}^2P_{3/2} - {}^2P_{3/2}$  transition at 134.7 nm is used in Cl fluorescence measurements. Monochromator slits are opened to 2 mm in order to obtain sufficient fluorescent signal intensities, resulting in a spectral resolution of approximately 2 nm. A typical detection efficiency for Cl is approximately  $1 \times 10^{-9}$  count s<sup>-1</sup>/ (molecule  $cm^{-3}$ ), with a background signal of about 2 counts s<sup>-1</sup>.

A mixture of  $Br_2$  in He—made by saturating 2 atm of He with Br<sub>2</sub> vapor at -78 °C—flows through a quartz lamp body<sup>17</sup> with a MgF<sub>2</sub> window. The mixture, at 1-2 torr in the lamp, is excited by microwave radiation. A sapphire window in front of the lamp serves to filter out short-wavelength emissions from any H, O, or N impurities. Without this filter, some  $Br_2$  is photolyzed in the lamp beam,<sup>16</sup> causing significant interference in the atom measurements. Slits are opened to 2 mm for measurements at 157.7 nm, the  ${}^{4}P_{5/2} - {}^{2}P_{3/2}$  transition.<sup>18</sup> The several nearby transitions of Br, at 157.5  $({}^{2}P_{3/2} - {}^{2}P_{1/2})$  and 158.3  $({}^{4}P_{1/2} - {}^{2}P_{1/2})$ nm, do not interfere with the measurement, since they connect to the spin-orbit excited state.<sup>18</sup> Any  $Br(^{2}P_{1/2})$  formed in this system is rapidly quenched in the presence of  $Br_2^{20}$  The detection efficiency for Br is similar to that for Cl.

Emissions to the ground state,  $Br(^{2}P_{3/2})$ , are apparently partially self-absorbed. The ratios of emission intensities from the same

- (19) Teilinghuisen, J.; Clyne, M. A. A. J. Chem. Soc. Faraday Trans. 2 1976, 72, 783.
- (20) Donovan, R. J.; Husain, D. Trans. Faraday Soc. 1966, 62, 2643.

<sup>(12)</sup> Brune, W. H.; Schwab, J. J.; Anderson, J. G. J. Phys. Chem. 1983, 97, 4503.

<sup>(13)</sup> Appelman, E. H.; Clyne, M. A. A. J. Chem. Soc., Faraday Trans. 1 1975, 71, 2072.

<sup>(14)</sup> Baulch, D. L.; Duxbury, J.; Grant, S. J.; Montague, D. C. J. Phys. Chem. Ref. Data 1981, 10, Suppl. 1.

<sup>(15)</sup> Schwab, J. J.; Anderson, J. G. J. Quant. Spectrosc. Radiat. Transfer 1982, 27, 445.

 <sup>(16)</sup> Clyne, M. A. A.; Cruse, H. W. Trans. Faraday Soc. 1971, 69, 2869.
 (17) Davis, D.; Braun, W. Appl. Opt. 1968, 7, 2071.
 (18) Clyne, M. A. A.; Townsend, L. W. J. Chem. Soc., Faraday Trans.

<sup>2 1974, 70, 1863</sup> 

TABLE I: Rate Constants Measured for OH + Cl<sub>2</sub> for Different Flow Tube Diameters and OH Sources

P, torr	i.d., cm	OH source	no. of rate measurements	$10^{14} k^{II a}$	$10^{14}s(k^{\rm II})^{b}$	$k^{\mathrm{I},c}$ s <sup>-1</sup>	$s(k^{\mathrm{I}}),^{d} \mathrm{s}^{-1}$	
3.12	1.6	$H + NO_2$	6	3.87	0.20	15.23	4.28	
9.95	1.6	$H + NO_2$	3	4.65	0.35	8.17	1.59	
0.44-5.86	2.5	$H + NO_2$	31	6.74	0.20	1.14	1.16	
3.15	2.5	$F + H_2O$	8	6.71	0.14	1.83	1.34	
1.05-3.10	3.2	$H + NO_2$	9	6.43	0.15	3.54	1.43	
0.44-5.86	е	both	48	6.70	0.12	1.48	1.16	

<sup>a</sup>Slope determined by least-squares fit; units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>b</sup>Standard deviation of the slope. <sup>c</sup>Intercept of least-squares fit. <sup>d</sup>Standard deviation of the intercept. <sup>e</sup>2.50- and 3.40-cm i.d.'s. This entry encompasses data from both  $H + NO_2$  and  $F + H_2O$  sources.

excited state to the spin-orbit slit ground substrates— $5s \ {}^{4}P_{3/2} - 4p^{5} \ {}^{2}P_{3/2}$  and  $-4p^{5} \ {}^{2}P_{1/2}$  (at 154.1 and 163.4 nm, respectively), and  ${}^{2}P_{3/2} - {}^{2}P_{3/2}$  and  $-{}^{2}P_{1/2}$  (at 148.9 and 157.5 nm, respectively)—are half the values predicted from the known oscillator strengths.<sup>18,19</sup> When the Br<sub>2</sub> mixing ratio is reduced by cooling the reservoir in liquid N<sub>2</sub>, the ratios agree with the oscillator strengths of the transitions.

Chemicals. The purity of the gases used are as follows: He (in lamps and all other discharges) 99.999%, He (bulk carrier) 99.995%,  $O_2$  99.99%,  $H_2$  99.999%,  $NO_2$  99.5%, NO 99.0% (further purified by passage through an ascarite trap), CF<sub>4</sub> 99.7%, and Cl<sub>2</sub> 99.9%—all obtained from Matheson. Br<sub>2</sub> (Fisher, 99.95%) is degassed in several freeze-pump-thaw cycles and further purified by vacuum distillation. In experiments where the Br<sub>2</sub> used has been degassed but not subjected to vacuum distillation, the measured rate constant is the same as when a more extensive purification procedure is followed. BrCl is prepared<sup>8</sup> by mixing a small amount of Br<sub>2</sub> (6-15 torr) in an excess of Cl<sub>2</sub> (80-260 torr), in initial ratios, [Cl<sub>2</sub>]/[Br<sub>2</sub>], of 2-20. The mixture is allowed to stand for at least 24 h to ensure that chemical equilibrium is reached.

## Results

First-order rate constants,  $k_{obsd}^{I}$ , are obtained from a leastsquares fit of the OH fluorescence data to

$$\ln S_{\rm OH} = {\rm constant} - k_{\rm obsd}^{\rm I} d \tag{16}$$

where  $S_{OH}$  is the net OH fluorescence signal, and d the distance from the sliding injector's tip to the OH fluorescence axis. d can be converted to time, t, under the plug flow approximation,<sup>9</sup> by  $t = d/\langle v \rangle$ , where  $\langle v \rangle$  is the bulk flow velocity in the reactor.  $k_{obed}^{I}$ in eq 16 can then be expressed in units of s<sup>-1</sup>.  $k^{I}$  is adjusted for radical loss on the sliding injector

$$k_{\text{net}}^{\text{I}} = k_{\text{obsd}}^{\text{I}} + k_{\text{probe}}^{\text{I}} \tag{17}$$

 $k_{net}^{I}$  is corrected for axial diffusion<sup>9</sup> by

$$k^{\rm I} = k^{\rm I}_{\rm net} (1 + k^{\rm I}_{\rm net} D / \langle v \rangle^2)$$
(18)

where D, in units of  $\text{cm}^2 \text{ s}^{-1}$ , is the diffusion coefficient of OH in He, taken to be 731/P; the pressure, P, is in torr.<sup>21</sup>

The bimolecular rate constant can be obtained from a leastsquares fit of  $k^{I}$  vs. the reactant concentration:

$$k^{\rm I} = k^{\rm II} [\text{reactant}] + \text{intercept}$$
(19)

the slope,  $k^{\text{II}}$ , being the second-order rate constant.

 $OH + Cl_2$ . We have studied reaction 1 over a pressure range from 0.44 to 9.95 torr in 57 experiments, all at 298 ± 3 K. Three different reactor i.d.'s and two different OH sources—H + NO<sub>2</sub> and F + H<sub>2</sub>O—are used. Data are obtained under conditions pseudo first order in OH: the initial [OH] is  $(1-2) \times 10^{11}$ molecules cm<sup>-3</sup>, and initial [Cl<sub>2</sub>]  $(1-30) \times 10^{14}$  molecules cm<sup>-3</sup>. OH decays are observed for 1–2 orders of magnitude. A typical set of OH decay curves is shown in Figure 3. Table I summarizes the rate data obtained in different flow tubes. No dependence on pressure is observed, except possibly in the 16 mm i.d. tube. The results from the 25 and 32 mm i.d. reactors, and both OH



Figure 3. Sample pseudo-first-order decays of OH for reaction 1.  $Cl_2$  concentrations are indicated in units of  $10^{14}$  molecules cm<sup>-3</sup>. In this example, p = 3.10 torr He, v = 559 cm s<sup>-1</sup>, in a 3.2 cm i.d. reactor. OH is made by H + NO<sub>2</sub>.



Figure 4. Plot of pseudo-first-order rate constants of OH decay vs.  $[Cl_2]$ . The data shown and the least-squares fit include the rate constant determinations made in 2.5 and 3.2 cm i.d. reactors, using H + NO<sub>2</sub> and F + H<sub>2</sub>O as OH sources, in 0.44-5.86 torr of He.

sources, are in excellent agreement with each other. In none of these cases is there a significant intercept. The 16-mm tube, however, provides results much lower than any other configuration, with large positive intercepts. The cause of this problem has not

<sup>(21)</sup> Plumb, L. C.; Ryan, K. R.; Barton, N. C. Int. J. Chem. Kinet. 1983, 15, 1081.

been satisfactorily determined. For a final determination of  $k_1$ , only the data from the two larger diameter tubes are used, shown in Figure 4. A least-squares analysis of the 48 data points yields

$$k_1 = (6.70 \pm 0.72) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The uncertainty includes estimates of potential experimental errors (all errors are quoted at the  $1\sigma$  level).

Attempts to measure the yield of Cl from reaction 1 by calibrating the Cl signal response by reactions 11 or 14 have not been successful, due to a very large difference between the net Cl wall losses within the detection chamber during calibration and run conditions. The loss in the detection chamber is measured to be about 50% in conditions of limiting radicals. It appears to be much smaller when radicals are in excess, such as during lamp calibration procedures. We interpret these results in terms of a model of surface-catalyzed recombination of Cl atoms followed by desorption of Cl<sub>2</sub>

$$2Cl \rightarrow Cl_2(surface)$$

$$Cl_2(surface) \rightarrow Cl_2(gas)$$

as has been suggested for heterogeneous atom recombination processes.<sup>22</sup> During calibrations, desorbed  $Cl_2$  is again available for reaction with excess H or F, reducing the apparent amount of Cl lost to the walls. During Cl yield measurements, however, the  $Cl_2$  formed on the wall disappears permanently, since now the radical concentration is limiting, and the reformed  $Cl_2$  is only a small fraction of the total  $Cl_2$  present. The difference in the wall losses under these different experimental conditions is difficult to measure precisely; any yield calculated from these experiments would be virtually meaningless due to the large error associated with it.

Instead, Cl yield of reaction 1 is made relative to the Cl yield of reaction 14, by quantitatively switching from H to OH by means of reaction 9. The H and OH concentrations are known from the calibration of the OH signal; in excess  $Cl_2$  complete conversion of H to Cl by reaction 14 is assumed.

Although the kinetic system is modeled via a computer kinetics simulation program (see below), it can be represented in a simple way by the following three reactions:

$$OH + Cl_2 \rightarrow Cl + HOCl$$
 (1a)

$$OH + Cl_2 \rightarrow ClO + HCl$$
 (1b)

$$Cl \rightarrow wall$$
 (wCl)

The rate of change of [Cl] is described by the differential equation

$$d[Cl]/dt = k_{1a}[OH][Cl_2] - k_{wCl}[Cl]$$
 (20)

The solution of eq 20, with boundary conditions at t = 0 of [OH] = [OH]<sub>0</sub> and [Cl] = 0, and the approximation of pseudo-first-order OH decay, is

$$[Cl] = \frac{(k_{1a}/k_1)[OH]_0}{k_{wCl}/k_{1a}[Cl_2] - 1} \{ \exp(-k_{1a}[Cl_2]t) - \exp(-k_{wCl}t) \}$$
(21)

where  $k_1 = k_{1a} + k_{1b}$ . If the wall loss is much slower than the formation step, the production of Cl is simply related to the first exponential of eq 21; plots of [Cl] vs. [Cl<sub>2</sub>] t should lie on the same curve. This result is only approximate when the wall loss is not negligibly small, or when secondary reactions contribute to the kinetics.

The effect of radical wall losses on the production of Cl differs somewhat from what this model suggests, as a consequence of the wall loss ordering  $k_{wOH} > k_{wH} > k_{wCl}$ ,  $k_{wBr}$ . Since the total time that radicals spend in the flow reactor is fixed, the wall loss apparent from observing a product form is

$$k_{\rm wNet} = k_{\rm wProduct} - k_{\rm wReactant}$$
(22)

In these experiments, as the reactant injector is pulled back, a



**Figure 5.** Production of Cl from reaction 1. Curves represent the computed [Cl] using the values of  $k_1$  presented, in units of  $10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The computation uses  $[H]_0 = 2.0 \times 10^{11}$ ,  $[NO_2]_0 = 2.0 \times 10^{12}$ , and  $[Cl_2]_0 = 4.0 \times 10^{14}$  molecules cm<sup>-3</sup>.

radical with a small wall loss (Cl or Br) replaces one with a larger loss (H or OH). Consequently,  $k_{wNet} < 0$ ; a wall "production" of Cl or Br arises, and the product signal in fact never reaches a maximum. This effect is naturally accounted for in a properly constructed computer simulation of the kinetics, as are other effects such as the greater amount of H than OH which survives passage down the flow tube, and the resulting differences in Cl production from reactions 1 and 14 (despite initially equal [H] and [OH]).

The Cl yield from reaction 1 is displayed in Figure 5 along with Cl production curves calculated from known reaction rate constants, various possible values of  $k_1$ , and experimentally determined wall loss rates of H, OH, and Cl. The time intercept in these measurements is determined empirically by extrapolating the initial Cl fluorescence signal rise back to zero, since the flow cross section varies within the detection chamber. The full list of reactions included in the computer simulation program used for these calculations, and a description of the integration method employed, are presented in the Appendix and supplementary material (see paragraph at end of text regarding supplementary material). Although the data are somewhat scattered, in part due to low fluorescence signals, they follow a production curve corresponding reasonably well to the measured rate of  $k_1$ , suggesting a branching ratio

$$k_{1a}/k_1 = 1.0 \pm 0.1$$

Since  $k_1$  and  $k_{14}$  are so disparate, Cl production from reaction 14 has been examined more closely, as shown in Figure 6, to ensure that the kinetics of this reaction are well understood. The Cl production agrees with reported values<sup>11</sup> of  $k_{14}$ .

When NO is added after reaction 1 is completed, no signal attributable to the conversion of ClO to Cl is observed. Thus

$$k_{1b}/k_1 < 0.01$$

within the experimental uncertainty. To verify that this conversion operates properly, ClO is prepared by reaction 4,  $O + Cl_2$ , using a large excess of  $Cl_2$  (>10<sup>15</sup> molecules cm<sup>-3</sup>) over O (10<sup>11</sup> molecules cm<sup>-3</sup>), in order to minimize the destruction of ClO by

$$O + ClO \rightarrow Cl + O_2$$
  $k = 5 \times 10^{-1}$ 

<sup>(22)</sup> Laidler, K. J. "Chemical Kinetics", 2nd ed.; McGraw-Hill: New York, 1965.

TABLE II: Rate Constants Measured for OH + Br<sub>2</sub> for Different Flow Tube Diameters and OH Sources

P, torr	i.d., cm	OH source	no. of rate measurements	$10^{11}k^{II}, a$	$10^{11}s(k^{\mathrm{II}})^b$	$k^{\mathrm{I}}, c \mathrm{s}^{-1}$	$s(k^{\mathrm{I}}),^{d} \mathrm{s}^{-1}$	
1.00-3.03	1.6	$H + NO_2$	14	5.69	0.28	-4.64	8.25	
1.03-5.88	2.5	$H + NO_2$	19	4.96	0.25	-0.79	6.23	
2.90-3.10	2.5	$F + H_2O$	12	4.93	0.15	2.25	3.31	
3.00	3.2	$H + NO_2$	5	5.07	0.15	2.16	3.12	
1.00-5.88	all	both	50	5.28	0.15	-2.50	3.64	

<sup>a</sup>Slope determined by least-squares fit; units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>b</sup>Standard deviation of the slope. <sup>c</sup>Intercept of least-squares fit. <sup>d</sup>Standard deviation of intercept.



**Figure 6.** Production of Cl from reaction 14. Curves represent the computed [Cl] using the values of  $k_{14}$  presented, in units of  $10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The computation uses  $[H]_0 = 2.0 \times 10^{11}$ , and  $[Cl_2]_0 = 3.0 \times 10^{12}$  molecules cm<sup>-3</sup>.

The ratio of ClO to Cl determined in this experiment is  $0.78 \pm 0.15$ , which is reasonable, considering the difficulty of preventing the secondary reaction from occurring.

 $OH + Br_2$ . We have studied reaction 2 from 1.01 to 5.81 torr, in 50 experiments at 298 ± 3 K, with the same variations in the flow tube diameter and OH sources, as used in the study of reaction 1. Mixing ratios of  $Br_2$  in He are also varied. Initial [OH] is  $(1-2) \times 10^{11}$  molecules cm<sup>-3</sup>; [Br<sub>2</sub>] used are within the range  $(2.1-68) \times 10^{11}$  molecules cm<sup>-3</sup>. Initial ratios of [Br<sub>2</sub>]/[OH] vary from 5 to 50.

Table II summarizes the rate determinations for reaction 2. No dependence on pressure is seen in any reactor arrangements. The various flow tube diameters and OH sources give values of  $k_2$  in good agreement with one another. Figure 7 presents the data graphed as  $k^{\rm I}$  vs. [Br<sub>2</sub>]. The combined result of all experiments, from an analysis of all 50 experiments, is  $k = (5.28 \pm 0.63) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

The ratio of Br produced to OH consumed by reaction 2 is found to be  $0.99 \pm 0.08$ . This value includes a 22% correction for the difference between Br loss within the detection chamber (primarily at the gap in the flow tube where OH is measured) during calibration of the Br fluorescence and during reaction. The wall loss during the calibration procedure is measured by discharging O<sub>2</sub> in the side arm and adding Br<sub>2</sub> through the injector. In the first 10 cm, the Br signal decays by 10% from its maximum. When Br atoms—formed from the discharge of Br<sub>2</sub>—are added through the injector, however, the Br level drops by 27% over the



Figure 7. Plot of pseudo-first-order rate constants of OH decay vs.  $[Br_2]$ . The data shown and the least-squares fit include the rate constant determinations made in 1.6, 2.5, and 3.2 cm i.d. reactors, using H + NO<sub>2</sub> and F + H<sub>2</sub>O as OH sources, in 1.00-5.88 torr of He.

same distance. We interpret this difference to arise from the heterogeneous recombination of Br atoms on the wall, followed by desorption of  $Br_2$ 

$$2Br \rightarrow Br_2(surface)$$

## $Br_2(surface) \rightarrow Br_2(gas)$

analogous to the case of Cl.

The Br yield of reaction 2 is also made relative to the Br yield of reaction 15, by quantitatively switching from H to OH by means of reaction 9. The H and OH concentrations are known from the calibration of the OH signal; complete conversion of H to Br in reaction 15 is assumed. The Br yields from reactions 2 and 15 are displayed in Figure 8 against Br production curves calculated from known reaction rates, various possible rates of reaction 2, and experimentally determined wall loss rates of H, OH, and Br. Details of the calculations are in the Appendix. Within the precision of the experiment, the yield of Br agrees with the measured  $k_{2}$ , and a branching ratio for channel 2a of

$$k_{2a}/k_2 = 1.0 \pm 0.1$$

The yield of BrO from channel 2b is determined by adding NO through the downstream loop injector, after reaction 2 is essentially complete. The lack of any Br fluorescence signal increase implies that

$$k_{2b}/k_2 < 0.01$$

according to the uncertainty of the measurement. To verify that

TABLE III: Rate Constants<sup>a</sup> for OH + BrCl Inferred from Halogen Mixing Ratios and Measured Rate Constants, k<sub>1</sub> and k<sub>2</sub>

[Cl <sub>2</sub> ]:[Br <sub>2</sub> ] <sup>b</sup>	slope $\pm \text{dev}^c$ intercept $\pm \text{dev}$	$k_1 f_1^d$	$k_2 f_2^e$	k <sub>3</sub> <sup>f</sup>	no. of expts	i.d., cm	press., torr
$5.03:2.80 \times 10^{-2}$	$2.98 \pm 0.07 \\ -0.28 \pm 0.87$	0.34	1.48	$1.16 \pm 0.17^{g}$	18	2.5	1, 3, 6
2.29:5.71 × 10 <sup>-2</sup>	4.77 ± 0.20 0.99 ± 3.25	0.15	3.02	1.60 ± 0.36	16	1.6 2.5 3.2	3 3 1,3
9.78:1.34 × 10 <sup>-2</sup>	$3.06 \pm 0.10$ -0.62 ± 2.38	0.65	0.71	$1.70 \pm 0.14$	8	1.6	6
$20.0:6.56 \times 10^{-3}$	$3.18 \pm 0.02$ $1.64 \pm 0.39$	1.34	0.35	$1.49 \pm 0.14$	7	2.5	3
av				$1.49 \pm 0.31^{a}$			

<sup>a</sup> Expressed in units of  $10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>b</sup> Equilibrium concentrations relative to [BrCl] = 1.0. <sup>c</sup> The slope and intercept, and their standard deviations from a least-squares fit of  $k^1$  against [BrCl]. <sup>d</sup> Contribution of OH decay by reaction 1;  $f_1 = [Cl_2]/[BrCl]$ . <sup>e</sup> Contribution of OH decay by reaction 2;  $f_2 = [Br_2]/[BrCl]$ . <sup>f</sup>  $k_3 = (slope - k_1[Cl_2] - k_2[Br_2])/[BrCl]$ . <sup>g</sup> Standard deviation of  $k_3$ , including the uncertainties in the slope,  $k_1$ , and  $k_2$ . <sup>h</sup> Standard deviation of the mean  $k_3$ .



Figure 8. Production of Br from reaction 2. Curves represent the computed [Br] using the values of  $k_2$  presented, in units of  $10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The computation uses [H]<sub>0</sub> =  $2.0 \times 10^{11}$ , [NO<sub>2</sub>]<sub>0</sub> =  $2.0 \times 10^{12}$ , and [Br<sub>2</sub>]<sub>0</sub> =  $2.0 \times 10^{12}$  molecules cm<sup>-3</sup>.

reaction 8 indeed quantitatively converts BrO to Br in this apparatus, O from a discharge of  $O_2$  is mixed with large excess of Br<sub>2</sub>, making BrO by reaction 12. NO is then introduced downstream of the reaction. The ratio of BrO to Br resulting from this procedure is  $0.94 \pm 0.09$ . Since reaction 13 contributes slightly to the presence of Br, to the detriment of BrO, this result agrees well with expectation.

OH + BrCl. Reaction 3 has been studied at 298  $\pm$  3 K, at pressures from 1 to 6 torr. The decay of OH is followed under pseudo-first-order conditions;  $[OH]_0 = (1-2) \times 10^{11}$  molecules cm<sup>-3</sup>, and  $[BrCl] = (1.5-46) \times 10^{12}$  molecules cm<sup>-3</sup>. The three flow tube diameters and two OH sources described above are used.

Since [BrCl] exists in equilibrium with  $[Br_2]$  and  $[Cl_2]$ , a single bimolecular rate constant cannot be obtained from a fit to an equation of the form of eq 20. Rather, the effects of all components of the mixture on the OH decay must be included:

$$k^{1} = k_{1}[Cl_{2}] + k_{2}[Br_{2}] + k_{3}[BrCl]$$
 (23)



Figure 9. Plot of first-order rate constants of OH decay vs.  $[Br_2]$ . The data shown and the least-squares fit include the rate constant determinations for two of the four halogen mixtures used. Conditions are presented in Table III.

Data have been obtained for four different mixtures of  $Br_2$ ,  $Cl_2$ , and BrCl. The He pressures and flow tube diameters have been varied systematically in these different gas mixtures: no differences in the reaction rate are noted. Figure 9 presents plots of  $k^{I}$  vs. [BrCl] for two different halogen mixtures.

Table III summarizes these data along with the results of one method of extracting  $k_3$  from the experiments. In this method, the equilibrium concentrations of the three halogen species are calculated from the equilibrium constant<sup>5</sup>

$$K_{\rm eq} = 7.63 = [{\rm BrCl}]^2 / ([{\rm Br}_2][{\rm Cl}_2])$$
 (24)

The contributions to the OH decay from reactions 1 and 2 are subtracted from the apparent second-order rate (the slope from a least-squares fit), leaving the rate constant attributable to reaction 3. This analysis yields

$$k_3 = (1.49 \pm 0.40) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

where the uncertainty is compounded from the statistical uncertainties of the measurements of  $k_1-k_3$  used in arriving at the final value of  $k_3$ , and an assessment of the possible systematic errors inherent in discharge flow experiments.

Individual product channels cannot be measured, since the two reactions consuming Cl14

Cl + Br<sub>2</sub> 
$$\rightarrow$$
 Br + BrCl  $k =$   
1.7  $\times$  10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (25)

and<sup>23,24</sup>

$$Cl + BrCl \rightarrow Br + Cl_2$$
  $k =$   
1.5 × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (26)

are much faster than the rate of Cl production from reaction 3. Reactions 25 and 26 do not, however, prevent the measurement of the production of X (Cl + Br) relative to XO (ClO + BrO)—i.e., (3a) + (3b) vs. (3c) + (3d). When NO is added downstream of the reaction, no increased Br signal is seen; thus

$$(k_{3c} + k_{3d})/k_3 < 0.01$$

within the measurement's limit of error.

#### Discussion

We compare our results to previous reaction rate constants and product measurements and calculate the rates of reverse reactions. From the context of atom-halogen molecule reactions, we estimate activation energies of the OH-halogen reactions and briefly examine the correlation between activation energies and electron affinities and ionization potentials of the reactants.

Literature Comparison. The rate of reaction 1 has been measured at 298 K by Leu and Lin,<sup>1</sup> and by Ravishankara, Eisele, and Wine.<sup>2</sup> Both groups studied this reaction using 2.5-cm flow reactors, producing OH by means of the  $H + NO_2$  titration, and following the OH decay by resonance fluorescence. Leu and Lin<sup>1</sup> determined that  $k_1 = (5.5 \pm 0.3) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Ravishankara et al.<sup>2</sup> found  $k_1 = 7.4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (no error limits were provided).

These two values of  $k_1$  are within about 20% of the value reported here,  $(6.70 \pm 0.70) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The wide variation in conditions-pressure, flow tube diameter, radical source, and reactant concentration-under which we have studied reaction 1, and the excellent agreement of these previous measurements with our own, indicate that  $k_1$  is well characterized at 298 K.

Neither Leu and Lin nor Ravishankara et al. carried out product determinations for reaction 1. Consequently, our measurement of the products from channels 1a (yield of  $1.0 \pm 0.1$ ) and 1b (yield < 0.01) stands alone; however, the measurement of the rate of the reverse reaction<sup>31,32</sup> is of considerable interest (see below). The lack of production of ClO is reasonable, despite channel 1b's greater exothermicity, since a highly constrained four-centered transition state

would be required along the reaction coordinate.

- (23) Clyne, M. A. A.; Cruse, H. W. J. Chem. Soc., Faraday Trans. 2 1972, 68, 1377.
- (24) Bemand, P. P.; Clyne, M. A. A. J. Chem. Soc., Faraday Trans. 2 1975, 71, 1132.
- (25) Yolles, R. S.; Wise, H. J. Chem. Phys. 1968, 48, 5109. (26) Veltman, I.; Durkin, A.; Smith, D. J.; Grice, R. Mol. Phys. 1980, 40, 213
- (27) Gorry, P. A.; Nowikow, C. V.; Grice, R. Mol. Phys. 1979, 37, 347.
  (28) (a) Parrish, D. D.; Herschbach, D. R. J. Am. Chem. Soc. 1973, 95, 6135.
  (b) Herschbach, D. R. Faraday Discuss. Chem. Soc. 1973, 55, 233.
  (29) Radlein, D. St. A. G.; Whitehead, J. C.; Grice, R. Mol. Phys. 1975, 575.
- 29, 1813
- (30) Durkin, A.; Smith, D. J.; Grice, R. Mol. Phys. 1982, 46, 1251.
  (31) Cook, J. L.; Ennis, C. A.; Leck, T. J.; Birks, J. W. J. Chem. Phys. 1981, 74, 545
- (32) Cook, J. L.; Ennis, C. A.; Leck, T. J.; Birks, J. W. J. Chem. Phys. 1981, 75, 497.

Using the discharge flow method, Poulet, Laverdet, and Le Bras<sup>3</sup> have studied reaction 2 at 298 K, monitoring OH by laser-induced fluorescence and by electron paramagnetic resonance. All experiments were conducted in about 0.45 torr of He. The two detection techniques gave a consistent rate constant,  $k_2 = (4.2)$  $\pm$  0.4)  $\times$  10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. A large intercept, 102  $\pm$  24 s<sup>-1</sup>, was also obtained. The value of  $k_2$  measured by Poulet et al. agrees with our own, (5.28 ± 0.50) × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, within the total uncertainty of the measurements.

Poulet et al. also measured the production of Br, observing both Br and OH by EPR. Their use of a double-concentric sliding injector greatly facilitated their measurement, allowing them to produce OH very near the EPR cavity, and then rapidly converting it to Br by adding Br<sub>2</sub>. They found  $k_{2a}/k_2 = 1.01 \pm 0.08$ , in agreement with our own work. In this case the four-center channel can be excluded.

Reverse Reaction Rates. With a knowledge of the forward rate. products, and thermodynamics of a reaction, one can infer the reverse rate of reaction, subject to two constraints: (1) whether the reaction is simple or complex, and (2) whether the reverse reaction has any other channels available. When a reaction is simple, proceeding with a single energy barrier via

$$OH + X_2 \rightleftharpoons X + HOX$$
 (27)

the equilibrium constant properly relates the forward and reverse rate constants. When a reaction is complex, the potential energy surface having a minimum along the reaction coordinate between reactants and products which stabilizes an intermediate

$$OH + X_2 \rightleftharpoons HOX_2 \rightleftharpoons X + HOX$$
 (28)

the equilibrium constant of the overall process may not relate to the observed forward and reverse rate constants,<sup>22</sup> if the intermediate is long-lived.

Evidence from molecular beam scattering experiments indicate that intermediates of some stability exist between the reactants and products for OH + Br<sub>2</sub>,<sup>26</sup> and the related reactions O +  $Cl_2$ ,<sup>27</sup>  $Br_{2}$ ,<sup>28,29</sup> and  $I_{2}$ .<sup>29,30</sup> Although the complexes exist long enough to be detected by molecular beam experiments, where the relevant time scale is the rotational period of the complex, they would have to have lifetimes longer than 10-100 ms, the time constants of chemical reaction in our bulk kinetics experiments, in order to invalidate the relationship between equilibrium and rate constants. RRK calculations indicate that the lifetime of HOBr<sub>2</sub> is only on the order of 1 ns. The nearly thermoneutral reaction 1a might be expected to pass through a much longer-lived intermediate, yet the predicted value of  $k_{1a}$  agrees well with the value actually measured (see below), implying that the intermediate is still relatively short-lived.

Using the available thermodynamic data,<sup>5,6</sup> we find for the reaction

$$Cl + HOCl \rightarrow OH + Cl_2$$
 (-1a)

 $k_{-1a} = 2.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The error bounds of  $k_{-1a}$ are approximately a factor of 2, due largely to the uncertainty of  $\Delta H_{\rm f}({\rm HOCl})$ . Cook et al.<sup>31</sup> have studied reaction -1a, following the decay of the reactant, HOCl, mass-spectrometrically, without observing the reaction products. They obtained  $k_{-1a} = (1.90 \pm$  $(0.35) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 300 \text{ K}$ . Our inferred value of  $k_{-1a}$  agrees well with their measurement. Although Cook et al. originally believed the products of reaction -1a to be HCl + ClO, they later realized<sup>32</sup> that the products more likely were OH + Cl<sub>2</sub>, when comparing their measurement of  $k_{-1a}$  to Leu and Lin's value<sup>1</sup> of the forward rate constant,  $k_1$ . The value of  $k_1$  measured by Leu and Lin implies that  $k_{-1a} = (2.1 \pm 0.1) \times 10^{-12} \text{ cm}^3$ molecule<sup>-1</sup> s<sup>-1</sup>, also in good agreement with Cook et al.

The reverse of reaction 2a

$$Br + HOBr \rightarrow OH + Br_2$$
 (-2a)

is endothermic and must be very slow:  $k_{-2a} = 2.4 \times 10^{-17} \text{ cm}^3$ molecule<sup>-1</sup> s<sup>-1</sup>, from calculations. The uncertainty of  $k_{-2a}$  is approximately a factor of 2, as a result of the strong dependence on  $\Delta H_{\rm f}({\rm HOBr})$ .

TABLE IV: Rate Constants and Activation Energies<sup>a</sup> for R + XY (R = Radical, X and Y = Halogens), Compared to the Electron Affinities of P and the Ionization Potentials of XY

		rate constant							
				BrCl		ICl			
radical	EA, <sup>b</sup> eV	F <sub>2</sub> (15.7 eV)	$Cl_2 (11.48 \text{ eV})^c$	$(11.1 \text{ eV})^c$	$Br_2 (10.53 \text{ eV})^c$	$(10.31 \text{ eV})^c$	IBr (9.98 eV) <sup>c</sup>	$I_2 (9.28 \text{ eV})^c$	
Cl	3.62	<0.5 <sup>e</sup>		140	1700	801			
Br	3.36	<0.3 <sup>e</sup>				0.3	350/		
F	3.34		1600 <sup>g</sup>		2200	3800 120 <sup>g</sup>		4800 <sup>g</sup>	
S OH O N	2.08 1.83 <sup>d</sup> 1.46 0.9	3.0 <sup>h</sup> 10 <sup>-9 i</sup> (18.4) 10 <sup>-18 k</sup> (10.4)	$ \begin{array}{c} 110^{h} (0.58) \\ 0.67^{j} \\ 0.42^{e} (2.72) \\ 0.0032^{j} (1.89) \end{array} $	1 <i>5<sup>j</sup></i> 230 <sup>e</sup> (0)	530 <sup>j</sup> 139 <sup>e</sup> (1) <sup>n</sup> 0.036 <sup>l</sup> (1.89)	0.002'	0.14 <sup>1</sup> (0.70)	0.24 <sup>m</sup> (0.070)	
Н	0.754	25 (2.40)	190 (1.17)		5400 (0.44)			3460 (0.431)	

"Recommended in ref 11, except where noted; rate constants are in units of 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>; activation energies (in parentheses) are in units of kcal mol<sup>-1</sup>. <sup>b</sup>Electron affinities are from ref 38, except where noted. <sup>c</sup>Ionization potential from ref 39. <sup>d</sup>Reference 39. <sup>e</sup>Reference 8. <sup>f</sup>References 23 and 24. <sup>g</sup>Reference 13; for F + ICl, 3800 and 120 are for the IF and CIF channels, respectively. <sup>h</sup>Reference 41. <sup>f</sup>References 35 and 36; rate constant is extrapolated below the reported temperature limits. <sup>1</sup>This work. <sup>k</sup>Reference 33; rate constant is extrapolated below the reported temperature limits. 'Reference 42. "Reference 43. "Reference 44.

Since we have not differentiated between channels 3a and 3b, the reverse reaction rates cannot be specified without additional information. Assuming that the less exothermic channel, producing HOBr + Cl, predominates-as a consequence of the "electronegativity ordering rule" which states<sup>28</sup> that in reactions H or O (as well as others) + XY, the less electronegative atom of XY lies in the center-the reverse rate for

$$Cl + HOBr \rightarrow OH + BrCl$$
 (-3b)

is  $k_{-3b} = 3.7 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

If other reaction channels such as

$$X + HOX \rightarrow XO + HX$$
 (29)

are available to the products X and HOX of reaction 27 or 28, then the reverse rate predicted by thermodynamics will, of course, differ from measurement. In the case of reaction 1, there does not appear to be a hydrogen-abstraction process

$$Cl + HOCl \rightarrow ClO + HCl \qquad \Delta H = -9.1 \text{ kcal mol}^{-1}$$
 (1c)

competing with reaction -1a, even though reaction 1c is more exothermic than reaction -1a.

Reactivity Correlations. We have observed a trend in OHhalogen reactivity:  $Br_2 > BrCl > Cl_2$ . Similar trends exist for numerous atom-halogen reactions.<sup>33,34</sup> While the ordering for these OH reactions happens to follow the same pattern as the reaction exothermicity, it breaks down when the reaction

$$OH + F_2 \rightarrow HOF + FO$$
 (30)

for which<sup>7</sup>  $\Delta H_r = -14$  kcal mol<sup>-1</sup>, is included. Reaction 30 is the most exothermic of these four halogen reactions, yet it has only been observed in flames<sup>35,36</sup> near 800 K (where the products are assumed to be HF + F + O), and appears to have a very large activation energy.

Table IV presents our results along with the rate constants of other reactions of radicals with halogens. In general, for each set of reactions of a radical with the different halogen and interhalogen molecules, the rate constant increases as the ionization potential of the halogen decreases. One exception to this trend is O + BrCl, which is faster than  $O + Br_2$ . Since the rate of the analogous reaction, OH + BrCl, lies between the  $Cl_2$  and  $Br_2$ reactions, and both O and OH react by abstracting Br to produce Cl, the cause of this small deviation is not explained. The reaction Cl + ICl also does not follow the trend. This is likely a consequence of the electronegativity ordering rule<sup>28</sup> mentioned above, as the more stable intermediate Cl-I-Cl does not result in a net (observable) reaction. Only the energetically less favored approach of Cl toward the more electronegative Cl end of ICl, resulting in the less stable Cl-Cl-I, can cause a reaction.

Table IV also shows the dependence of the reaction rate on the electron affinity of the radical. For each halogen or interhalogen molecule (with the exception of BrCl), the reaction rate constant increases along with the electron affinity of the reacting radicals N, O, OH and S. The reactions involving F, Cl, and Br follow the same trend, with several exceptions, one being the reaction of Cl with ICl mentioned above. H atoms, however, react much more rapidly than the correlation suggests. This may be due to a reaction mechanism for H different from that for other radicals: molecular beam experiments indicate that  $H + X_2$  reactions are very impulsive, in many ways analogous to photodissociation,<sup>28b</sup> and unlike O and  $OH + X_2$  which pass through long-lived intermediates.<sup>26-30</sup>

Several attempts have been made to correlate the variations in activation energy with the polarizability of the reactants. Krech and McFadden suggest that a correlation should be made with the polarizability<sup>34</sup>—in particular, that the activation energy,  $E_{act}$ , can be expressed as

$$E_{\rm act} = C/\alpha_{\rm X_2} \tag{31}$$

where  $\alpha_{X_2}$  is the polarizability of molecule  $X_2$ , and C is an empirical constant. The observed activation energies for the reactions  $O + F_2$ ,  $Cl_2$ ,  $Br_2$ , and  $I_2$  of 10.4, 3.3, 1, and 0 kcal mol<sup>-1</sup>, respectively,<sup>33</sup> agree with the trend in polarizabilities. The activation energies of many other radical-molecule reaction families also correlate with the polarizability of the molecule.

Spirin<sup>37</sup> proposes a relationship between  $E_{act}$  and the polarizabilities of the atomic reactants and products of the reaction A + BC  $\rightarrow$  AB + C, based on an empirical extension of London's equation<sup>22</sup> for the energy of a triatomic system:

$$E_{\rm act} = d(0.75D_{\rm AC} - q)(\alpha_{\rm A}^{-1} + \alpha_{\rm C}^{-1})$$
(32)

where  $D_{AC}$  is the bond energy of AC, q the reaction exothermicity, and d an empirical parameter. The polarizability dependence of eq 32 agrees qualitatively with our results combined with the data of Table IV.

<sup>(33)</sup> Krech, R. H.; Diebold, G. J.; McFadden, D. L. J. Am. Chem. Soc. 1977, 99, 4605.

<sup>(34)</sup> Krech, R. H.; McFadden, D. L. J. Am. Chem. Soc. 1977, 99, 8402.
(35) Streng, D. G. Combust. Flame 1962, 6, 89.
(36) Nosvoa, V. V.; Lovachev, L. A.; Vedeneev, V. I. Combust. Flame

<sup>1964, 8, 163.</sup> 

<sup>(37)</sup> Spirin, Yu. L. Russ. J. Phys. Chem. (Engl. Transl.) 1962, 36, 636. (38) Hotop, H.; Lineberger, W. C. J. Phys. Chem. Ref. Data 1975, 4, 539.

<sup>(39)</sup> Franklin, J. L.; Dillard, J. G.; Rosenstock, H. M.; Herron, J. T.; Draxl, K.; Field, F. H. "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions"; U.S. Department of Commerce:

Washington, DC, 1969; NSRDS-NBS26. (40) Weast, R. C., Ed. "Handbook of Chemistry and Physics", 54th ed.;

CRC Press: Cleveland, OH, 1973. (41) Clyne, M. A. A.; Townsend, L. W. Int. J. Chem. Kin., Symp. Ed. 1, 1975, 73.

<sup>(42)</sup> Grigor, M. R.; Phillips, L. F. Symp. (Int.) Combust., [Proc.] 1967, 11, 1171

<sup>(43)</sup> Phillips, L. F. Can. J. Chem. 1965, 43, 369.

<sup>(44)</sup> Moin, F. B.; Yurkevich, Ya. P.; Drogo'itskii, V. M. Dokl. Akad. Nauk SSSR 1976, 226, 866.

While the activation energies and polarizabilities do follow an empirical correlation, a more fundamental relationship appears when the energetics of the reactive process are considered at a molecular level. As the reactants, R and XY, approach to pass over an energy barrier defining the transition state, a new bond between the radical and molecule is formed: R-XY. Electronic charge from XY can be envisioned to move between R and X, creating, for a time, a charge imbalance among the atoms

$$R-(XY)^+$$
 or  $R-X^+-Y$ 

The ability to stabilize the initial charge imbalance increases-that is, the transition state complex is stabilized-with the increasing electron affinity of R and the decreasing ionization potential of XY (particularly of X). The dependence of the activation energy on the electron affinities of the terminal radicals or atoms has been noted by Benson.<sup>7</sup>

Since the correlation depends more on the electron affinity and the ionization potential than on the overall reaction exothermicity, as is evidenced by the O and OH +  $F_2$  reactions, the reaction barrier likely occurs before the X-Y bond is significantly altered. This agrees well with the inference from molecular beams experiments of a stable RXY intermediate, in which the X-Y bond is not yet broken. The rapidity of the  $H + X_2$  reactions can be explained in part by their different mechanisms: the absence of a stable intermediate means that the HX bond is formed and X-X bond broken to a much larger extent in the transition state, overcoming the dependence on the electron affinity of the radical.

It is unlikely that a temperature-dependent study will be carried out for reaction 3, due to the equilibrium of Br<sub>2</sub>, Cl<sub>2</sub>, and BrCl that complicates the analysis. In light of the evidence that the ionization potential is a factor determining the activation energy, and considering the large magnitude of  $k_2$ , we hypothesize that  $E_2 = 0$ , where  $E_i$  is the activation energy of reaction *i*. If the frequency factors,  $A_i$ , in the Arrhenius expressions,  $A_i$  exp- $(-E_i/RT)$ , for reactions 2 and 3 are equal, the difference between  $k_2$  and  $k_3$  can be attributed to  $E_3$ . On this basis we suggest that  $E_3 = 2.1$  kcal mol<sup>-1</sup>. If the same conditions apply to reaction 1, then  $E_1 = 3.4 \text{ kcal mol}^{-1}$ .

We are interested in extending our work on OH-halogen reactions to include I<sub>2</sub>, ICl, and IBr. We expect these reactions to be at least as rapid as  $OH + Br_2$ . The electron affinity of SH is larger than that of either OH or S; provided that the halogen reactions with SH are exothermic, we expect that the as yet unexplored SH-halogen reactions will test the effects of a radical's electron affinity on its reactivity.

Acknowledgment. We thank Dr. Glenn D. Graham for his help in the early phases of this work and Dr. James J. Schwab for providing us with a chlorine lamp. This work has been supported by the National Science Foundation under Grant ATM-8115112.

## Appendix

Simulations are performed by using the Runge-Kutta algorithm.<sup>45</sup> The substantial reaction set includes 57 bimolecular reactions-representing the radical-radical and radical-molecular reactions of the various species present (including H, H<sub>2</sub>, OH, Cl, ClO, Cl<sub>2</sub>, HOCl, Br, BrO, Br<sub>2</sub>, HBr, HOBr, NO, and NO<sub>2</sub>); 15 termolecular reactions-representing various radical recombination steps, at the low-pressure limit-forming species such as HNO<sub>3</sub>, CINO, CINO<sub>2</sub>, CINO<sub>3</sub>, BrNO, BrNO<sub>2</sub>, and BrNO<sub>3</sub>; and 5 unimolecular reactions-accounting for the loss of radicals at the reactor wall. The rate constants of these reactions are largely obtained from ref 10.

Registry No. OH, 3352-57-6; Cl<sub>2</sub>, 7782-50-5; Br<sub>2</sub>, 7726-95-6; BrCl, 13863-41-7.

Supplementary Material Available: A description of the computational scheme employed and a listing of all the reactions and rate constants used in it (5 pages). Ordering information is given on any current masthead page.

(45) Milne, W. E. "Numerical Solution of Differential Equations"; Dover: New York, 1970.

# Adduct Formation and Absolute Rate Constants in the Displacement Reaction of Thiyl **Radicals with Disulfides**

## M. Bonifačić and K.-D. Asmus\*

Hahn-Meitner-Institut für Kernforschung Berlin, Bereich Strahlenchemie, D-1000 West Berlin 39, Federal Republic of Germany (Received: June 5, 1984)

The displacement reaction of thiyl radicals with disulfides is shown to proceed via a transient adduct radical by using time-resolved pulse radiolysis techniques. The relatively long-lived adduct  $(t_{1/2} > 100 \ \mu s)$  formed in the forward reaction of the equilibrium  $RS + RSSR \Rightarrow \{RSS(R)SR\}$  is suggested to be a sulfuranyl radical with the unpaired electron located in an antibonding  $\sigma^*$  orbital within a trisulfide bridge. These species exhibit optical absorptions in the UV, e.g.,  $\lambda_{max} = 375 \pm 10$  nm and  $\epsilon = (3.4 \pm 0.4) \times 10^3$  M<sup>-1</sup> cm<sup>-1</sup> for the all-methylated radical, and have been identified in aqueous and methanolic solutions. Equilibrium constants of  $K = 180 \pm 30$  and  $60 \pm 20$  M<sup>-1</sup> have been evaluated for the systems with R = CH<sub>3</sub> and cysteine residue, respectively, via two different methods. The corresponding forward reactions occur with  $k(RS + RSSR) = 3.8 \times 10^6$  and  $7.7 \times 10^5 M^{-1} s^{-1}$ , respectively.

## Introduction

Chemical systems containing different disulfides or disulfidethiol mixtures are known to undergo relatively rapid exchange of thiyl groups resulting in the formation of mixed disulfides<sup>1,2</sup> as outlined in the general equilibria 1 and 2. Since disulfides

> $R^{1}SSR^{1} + R^{2}SSR^{2} \Rightarrow 2R^{1}SSR^{2}$ (1)

 $R^{1}SSR^{1} + R^{2}SH \Rightarrow R^{1}SH + R^{1}SSR^{2}$ (2)

and thiols serve important biochemical functions, these exchange

reactions have always found particular interest in biological sciences.<sup>3</sup> It is now well established that these processes involve thiyl radicals which act via an overall substitution mechanism, e.g.

Gupta, D.; Knight, A. R. Can. J. Chem. 1980, 58, 1350.
 Owen, T. C.; Ellis, D. R. Radiat. Res. 1973, 53, 24 and references cited therein.

<sup>(3)</sup> Friedman, M. "The Chemistry and Biochemistry of the Sulfhydryl Group in Amino Acids, Peptides and Proteins"; Pergamon Press: Oxford,