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# Infrared chemiluminescence studies of H atom reactions with $Cl_2O$ , CINO, $F_2O$ , $CF_3OF$ , $CIO_2$ , $NO_2$ , and CIO

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Infrared chemiluminescence from the HF, HCl, and OH products has been used to measure the nascent vibrational distributions and the rate constants at 300 K for the title reactions in a fast flow reactor. The ClO reaction was observed as a secondary step in the ClO<sub>2</sub> and Cl<sub>2</sub>O systems. The reactions proceeding by a direct mechanism, Cl<sub>2</sub>O, ClNO, OF<sub>2</sub>, and CF<sub>3</sub>OF release relatively small fractions,  $\sim 0.37$ , of the available energy as HCl or HF vibrational energy with narrow distributions, in accord with the dynamics associated with the H atoms on a repulsive potential surface. The ClO<sub>2</sub> and NO<sub>2</sub> reactions, which proceed by short lived intermediates, release a larger fraction of vibrational energy to OH and with broad distributions. Although the data for the ClO reaction are not definitive, the OH formation channel is the more important by a factor of 4–5. The NO<sub>2</sub> reaction was studied in direct comparison with Cl<sub>2</sub> to choose the best Einstein coefficients of OH by comparing the OH and HCl formation rate constants.

# I. INTRODUCTION

This laboratory has studied reactions yielding HX (X = F, Cl, Br, O) products by infrared chemiluminescence (IRCL),<sup>1-3</sup> using the arrested-relaxation (AR) and, more recently, the fast flow reactor (FR) techniques to observe H atom abstraction by F, Cl, and O atoms<sup>2,4</sup> and H atom reactions with halogens and halogen containing polyatomic molecules.<sup>5-8</sup> With the exception of a few F atom reactions, the nascent HX(v) distributions obtained from the two techniques are in agreement.<sup>4(a),8</sup> One advantage of the flow reactor is that the reagents are homogeneously mixed for Boltzmann conditions, which allows product formation rate constants to be measured by comparison to a reference reaction. In this study the FR technique was used to measure the nascent HX vibrational distributions and the product formation rate constants for H atom reactions with Cl<sub>2</sub>O, ClNO, F<sub>2</sub>O, CF<sub>3</sub>OF, ClO<sub>2</sub>, NO<sub>2</sub> and the ClO radical. Since the initial goal was to study the H + ClO reaction as a secondary step from Cl<sub>2</sub>O and ClO<sub>2</sub>, these primary reactions were studied in detail.<sup>9(a)</sup> The ClNO, OF<sub>2</sub> and CF<sub>3</sub>OF reactions were studied earlier,<sup>9(b)</sup> and those results have been mentioned in a review chapter.<sup>1</sup> Preliminary results for ClO<sub>2</sub> and NO<sub>2</sub> were communicated in describing the FR technique for reactions giving OH, but new measurements are reported here with an emphasis on measuring the NO<sub>2</sub> rate constant so that the best OH Einstein coefficients can be identified. The thermochemistry of all reactions is summarized in Table I of Sec. III. The ClO reaction is especially interesting because the HCl + O( ${}^{3}P$ ) and OH + Cl exit channels have nearly the same available energy; the HCl and  $O(^{1}D)$  channel is 8 kcal mol<sup>-1</sup> endoergic and can be neglected.

The H atom reactions studied by the IRCL technique include halogens  $(X_2)$ , interhalogens (XX'), and a few polyatomic halides (XR), notably the sulfur halides.<sup>1,8</sup> Reactions taking place by a direct mechanism give a modest  $\langle f_V(HX) \rangle$  and low  $\langle f_R(HX) \rangle$ .<sup>1,7,8</sup> A macroscopic branch, as well as microscopic branch with two different dynamical

pathways contributing to the more exoergic channel (HX), is observed for the interhalogens.<sup>1,5,11</sup> The microscopic branch was identified from the two component nature of the rotational distribution; the low J component corresponds to the direct attack on X and the high J component arises from the initial attack on X' with subsequent migration to the X atom. Except for SCl<sub>2</sub>, the energy disposal for the RX reactions resembles the  $H + X_2$  reactions.<sup>1,8</sup> The rotational distribution from SCl<sub>2</sub> has two components,<sup>8</sup> and the dynamics are thought to resemble the XX' reactions. The H atom reactions proceeding over a repulsive potential surface have some common general features associated with the rapid motion of the light H atom: (1) the  $\langle f_V \rangle$  and  $\langle f_R \rangle$  are small and  $\langle f_T \rangle$  is large, especially when compared to H atom abstraction reaction by F, Cl or O atoms,<sup>2,4</sup> (2) the highest observed HX(v,J) level is below the thermochemical limit, and (3) the vibrational surprisal plots are nonlinear.<sup>7</sup> The present work shows that the ClNO, Cl<sub>2</sub>O, CF<sub>3</sub>OF, and F<sub>2</sub>O reactions also display these general dynamical features.

The ClO<sub>2</sub>, NO<sub>2</sub>, and ClO reactions represent a different class of systems. Laser-induced fluorescence,13 molecular beam measurements,<sup>14</sup> and IRCL studies<sup>8,10,15</sup> of NO<sub>2</sub> give  $\langle f_V(\text{OH}) \rangle = 0.25, \langle f_R(\text{OH}) \rangle = 0.22, \langle f_T \rangle = 0.25, \text{ and},$ by difference,  $\langle f_{V,R}(NO) \rangle = 0.28$ . The present work, which provides a more definitive assignment of the OH(v,J)distributions from  $ClO_2$ , <sup>10,13(a)</sup> shows that the OH(v) distributions from both ClO<sub>2</sub> and ClO are broad with  $\langle f_V \rangle \approx 0.45$ . These results are consistent with dynamics associated with a short-lived intermediate. The secondary reactions from the  $Cl_2O$  (to observe the OH channel) or the  $ClO_2$  (to observe the HCl channel) systems were used to investigate the ClO reaction. In a subsequent paper,<sup>16</sup> the vibrational distributions and the branching ratio obtained here will be shown to agree with experiments in which the ClO reaction was studied as a primary step.

Perona<sup>17</sup> reported IRCL studies of the  $F_2O$  and  $Cl_2O$  reactions, but the present experiments represent substantial improvement in technique. The ClNO reaction has been

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studied by the AR method,<sup>18</sup> by molecular beams,<sup>19</sup> and by the FR technique in Kaufman's laboratory;<sup>20</sup> all results are in broad agreement. The rate constants for  $Cl_2O$  and ClNOare similar to that of  $Cl_2$ , but the rate constants for  $OF_2$  and  $CF_3OF$  are three orders of magnitude smaller.

New Einstein coefficients  $(A_{v,J})$  were used for HCl.<sup>21(b)</sup> Although the relative values of the new  $A_{v,J}$  (HCl) for the  $\Delta v = 1$  transitions did not change, the absolute values increased by factors of 1.16, 1.20, 1.21, and 1.25 for v = 1, 2, 3, and 4, respectively. The reliability of the OH Einstein coefficients has been extensively examined.<sup>10,22-24</sup> Recently, Langhoff *et al.* (LWR)<sup>24</sup> have published  $A_{v,J}$  (OH) values based on the improved dipole moment function of Werner *et al.*<sup>21(c)</sup> The OH formation rate constants for the ClO<sub>2</sub> and NO<sub>2</sub> reactions were determined, relative to H + Cl<sub>2</sub>, using the Einstein coefficients of both LWR<sup>24</sup> and Mies.<sup>22</sup> The rate constants calculated using the  $A_{v,J}$  (OH) values of LWR were in better agreement with the currently recommended NO<sub>2</sub> rate constant.

#### **II. EXPERIMENTAL TECHNIQUES**

# A. Flow reactor and detection of chemiluminescence

All reactions were studied in either of two flow reactors<sup>2,9(a)</sup> using  $\sim 0.7$  Torr of Ar carrier gas at room temperature. These reactors, which were constructed of Pyrex glass tubes of either 4 or 5 cm diameter, were connected to a Roots blower backed up by a mechanical pump. The inlets for the H atoms and Ar buffer gas were placed at the entrance of the reactor. The H atoms were produced by passing a H<sub>2</sub>/Ar mixture through a microwave discharge (2450 MHz, 60 W) and introduced into the reactor through a 8 mm diameter Pyrex tube placed concentrically with the perforated ring inlet for Ar. The discharge tube and flow reactor were treated with phosphoric acid to minimize the H atom loss. The tank grade (99.998%) Ar was purified by passage through two molecular sieve filled traps at -77 °C and then another sieve filled trap at -198 °C. After each experiment, the traps were regenerated by heating to  $\sim 250$  °C under vacuum. The flow rates of the reagents and H<sub>2</sub> were monitored by calibrated capillary oil flow meters. The total Ar flow was distributed in three lines, 10% through the H atom line, 10% through the reagent line, with the rest added to the reactor. The individual Ar flows were monitored by three Fischer-Porter triflat flowmeters, which were calibrated using a wet test meter.

The reagent was added through a ring inlet with holes on the inner surface which was placed just before the observation window fitted with NaCl disks. The window was  $\sim 20$ cm downstream from the H-atom inlet. The typical reaction times (hereafter designated as  $\Delta t$ ) in the 4 and 5 cm reactors were 0.15 and 0.35 ms, respectively. The CF<sub>3</sub>OF and F<sub>2</sub>O reactions, which are about three orders of magnitude slower than the other reactions were studied only in the large diameter reactor; however, several of the other reactions were studied in both reactors. The reagent lines and storage bulbs for F<sub>2</sub>O and CF<sub>3</sub>OF were of stainless steel. All other reagents were stored in 12  $\ell$  Pyrex glass bulbs as 10% mixtures in Ar and were further diluted with Ar when introduced into the reactor.

The infrared spectra were recorded at 1 cm<sup>-1</sup> resolution with a Digilab (FTS-20) FTIR spectrometer equipped with a cooled (-196 °C) InSb detector. The intensities for each transition were converted to relative vibrational populations using the  $A_{v,J}$  values<sup>21,24</sup> and the response function of the detector/optical system, which was obtained from a standard black-body source. Absolute  $A_{v,J}$  values are required for determining rate constants for reactions giving HF or OH when  $H + Cl_2$  is the reference reaction. Under our experimental conditions, the populations in the low and intermediate rotational levels of HCl, OH and HF relax to a 300 K Boltzmann distribution. However, populations in levels above J = 8 of HF can be easily observed, if they are formed by a given reaction.<sup>4</sup> The rotational relaxation of HCl in Ar is more rapid than for HF and only Boltzmann distributions are normally observed; however, if HCl  $(J \ge 15)$  are formed, they can be observed.<sup>6</sup> The rotational relaxation rates for OH(J) are intermediate and small populations in levels  $J \ge 8$ were observed in this work from  $ClO_2$  in OH(v = 1 and 2)and from NO<sub>2</sub> in OH(v = 1).

## **B. Reagents**

Since  $ClO_2$  and  $Cl_2O$  are sensitive to light and shock, the glass storage bulbs were enclosed in wire-mesh screen boxes and covered with black cloth, the reagent lines were covered with aluminum foil, and experiments were carried out in a dark laboratory. As already noted,  $F_2O$  and  $CF_3OF$  were handled in stainless steel lines and stored in stainless steel reservoirs.

Our procedure for generating ClO<sub>2</sub>, which was a slight modification over the standard procedure,<sup>25</sup> consisted of passing a Cl<sub>2</sub>/air mixture over NaClO<sub>2</sub> flakes packed in a 20 in. long, 3/4 in. diameter glass column. Flows of 5 and 250  $cm^3 min^{-1}$  of  $Cl_2$  and air, respectively, were passed through the column for about 1-1/2 h with collection of the products at 196 °C. The products were distilled under vacuum to remove impurities, mainly water and Cl<sub>2</sub>, and ClO<sub>2</sub> was collected in a trap cooled to -98 °C (CH<sub>3</sub>OH slush bath). The purity was found to be better than 95% by UV absorption. Cl<sub>2</sub>O was prepared from the static reaction between yellow HgO and  $Cl_2$  at -78 °C.<sup>26</sup> The dry, yellow HgO powder was placed in a round bottom flask and the Cl<sub>2</sub> was condensed into this reactor at -196 °C for a Cl<sub>2</sub>:HgO ratio of 2. The reactor was warmed to -40 °C (trichloroethylene/dry ice) for  $\sim 10$  h, then the products were pumped through two traps maintained at -112 and -196 °C. The Cl<sub>2</sub>O was collected at -112 °C as a dark cherry colored liquid. The purity, as checked by UV absorption, was ≥95%. The CINO was prepared using a standard procedure.<sup>25(a)</sup> CF<sub>3</sub>OF was synthesized by the fluorine chemistry group at KSU. The F2O was purchased from K&K Laboratories Inc., Plainview, NY.

#### C. Measurement of the fractional dissociation of H<sub>2</sub>

The reaction of  $Ar({}^{3}P_{2,0})$  atoms with  $H_{2}$  gives an emission ( $H_{2}^{*} + ArH^{*}$ ) from 220 to 440 nm,<sup>27</sup> which is first or-

der with respect to  $[H_2]$  for short reaction times ( $\leq 0.3 \text{ ms}$ ) and low  $[H_2]$ . The fractional dissociation of  $H_2$  by the MW discharge was determined by monitoring the reduction of the intensity of the ArH\* + H<sup>\*</sup> emission intensity when the MW discharge was turned on, see Fig. 1. For this experiment the reagent line of the flow reactor was replaced with a small Ar( ${}^{3}P_{2,0}$ ) atom generator.<sup>28</sup> The Ar( ${}^{3}P_{2,0}$ ) flow was added into H/H<sub>2</sub>/Ar bulk flow just before the observation window (the NaCl disk was replaced with a quartz disk). The fractional dissociation was  $0.88 \pm 0.02$  for  $[H_2] \leq 10^{13}$ molecule cm<sup>-3</sup>.

## **III. RESULTS**

#### A. Thermochemistry

Table I summarizes the thermochemistry. The  $D_0$  (Cl-NO),  $D_0$  (ClO-O), and  $D_0$  (ClO-Cl) values are well established<sup>29</sup> and  $D_0$  (Cl-O) is very precisely known.<sup>30,31</sup> Although quoted with a small uncertainty,  $D_0$  (CF<sub>3</sub>O-F)<sup>32</sup> probably is less well known than the preceding cases. The reported  $D_0$  (FO-F)<sup>33</sup> values range from 37.0 to 43.0 kcal mol<sup>-1</sup>, with 40 kcal mol<sup>-1</sup> being a compromise value. The activation energies, if they had not been measured were assigned from the product formation rate constants measured in this work and the  $E_a = 1.2$  kcal mol<sup>-1</sup> for the H + Cl<sub>2</sub> reaction,<sup>29</sup> after adjusting the preexponential factors for the number of available halogen atoms. Since, the internal excitation of the HCl or HF products from H atom reactions seldom extend to the thermochemical limit, the IRCL data cannot be used to establish bond energies.

# B. HCI(v) distribution from Cl<sub>2</sub>, Cl<sub>2</sub>O, and CINO

The  $Cl_2$  reaction was studied for a range of  $[H_2]$  and  $[Cl_2]$  to establish the  $[H_2]$  and  $[Cl_2]$  for which HCl(v)



FIG. 1. Plot of  $ArH^* + H_2^*$  emission intensity vs  $[H_2]$  with,  $\blacksquare$ , and without,  $\bullet$ , the microwave discharge on the  $H_2$  line. The emission was monitored at 289 nm with a 0.5 m monochromator and photomultiplier tube.

TABLE I. Summary of thermochemistry (kcal mol<sup>-1</sup>)

Reagent	$D_0(\mathbf{R}-\mathbf{X})$	$E_a$	$\langle E \rangle^{a}$	Ref.	
Cl <sub>2</sub>	57.1 ± 0.01	$1.2 \pm 0.1$	47.9 ± 0.1	30	
Cl <sub>2</sub> O	$33.3 \pm 2.0$	$0.8 \pm 0.5$	$71.6 \pm 2.5$	29	
NÕCI	37.1 + 1.0	0.8 + 0.3	67.7 + 1.5	29	
F,0	$40.0 \pm 4.0$	~5.5	$102.7 \pm 4.0$	33	
CF,OF	$43.5 \pm 1.0$	~4.6	$98.3 \pm 2.0$	32	
NO <sub>2</sub>	71.8 + 0.2	0.5 + 0.5	31.5 + 0.5	29	
Cl0,	$58.2 \pm 2.0$	0.6 + 0.5	45.5 + 2.5	29	
CIO	64.6 + 0.02	0.5 + 0.5	$39.7 + 1.0^{\circ}$	31	
	_	$0.5 \pm 0.5$	$38.7 \pm 1.0^{\circ}$		

<sup>a</sup>  $\langle E \rangle = D_0 (H-X) - D_0 (R-X) + E_a + (n/2) RT; n = 5$  for diatomic regents and n = 6 for polyatomic reagents. See text for method of assignment of  $E_a$  values.

<sup>b</sup>Available energy for the HCl channel.

<sup>c</sup> Available energy for the OH channel.

relaxation was unimportant for 0.15 and 0.11 ms reaction times. Results from several experiments are shown in Table II. The HCl(v) distribution did not show any dependence on [Cl<sub>2</sub>] or [H<sub>2</sub>] for concentrations  $<1.5 \times 10^{13}$  or  $<2 \times 10^{13}$ molecules cm<sup>-3</sup>, respectively. For the highest [H<sub>2</sub>] used, which was  $3.7 \times 10^{13}$  molecule cm<sup>-3</sup> in experiment Cl<sub>2</sub>-3, the HCl(v) distribution was slightly relaxed (P<sub>1</sub>-P<sub>4</sub> = 16:42:35:07) compared to the best distribution (P<sub>1</sub>-P<sub>4</sub> = 12:38:40:10). The nascent distribution for Cl<sub>2</sub> has been cited as P<sub>1</sub>-P<sub>4</sub> = 14:40:40:05 based upon an extensive series of AR experiments.<sup>8</sup> However, the present data, which were collected over a five year period, always showed a significantly higher v = 4 population, and we favor  $P_1-P_4$ =  $12 \pm 1:38 \pm 2:40 \pm 2:10 \pm 1$  as the nascent distribution.

The HCl(v) rotational distributions were 300 K Boltzmann for both the Cl<sub>2</sub> and Cl<sub>2</sub>O reactions. In expt Cl<sub>2</sub>O-1 the  $[H_2]$  was 5.3×10<sup>12</sup> molecule cm<sup>-3</sup> and [Cl<sub>2</sub>O] was varied from 1.2 to  $3.4 \times 10^{12}$  molecule cm<sup>-3</sup>; Fig. 2 shows that  $P_V$ did not depend on [Cl<sub>2</sub>O] in this range. Another experiment was done with  $[H_2] = 22 \times 10^{12}$  molecule cm<sup>-3</sup> and  $[Cl_2O]$ was varied from  $1.4 \times 10^{12}$  to  $3.1 \times 10^{12}$  molecule cm<sup>-3</sup>; the HCl(v) distribution did not show any significant change. The distribution obtained from the average of the experiments with  $[H_2] \leq 22 \times 10^{12}$  and  $[Cl_2O] \leq 3.4 \times 10^{12}$  molecule cm $^{-3}$  $P_1 - P_5 = 9 \pm 0.4:28 \pm 1.0:41 \pm 1.0:19$ was  $\pm$  0.8:3  $\pm$  0.2. Entry Cl<sub>2</sub>O-4 in Table II gives the results from an experiment in the larger reactor ( $\Delta t = 0.35 \text{ ms}$ ), the HCl(v) distribution,  $P_1-P_5 = 12:31:38:17:02$ , is within the experimental uncertainty of the distribution obtained from experiments in the smaller diameter reactor. This comparison, as well as the similarity of the results for the Cl<sub>2</sub> reaction in the two reactors, confirms the reliability of the early work.9(b)

A plot of the  $P_V$  vs  $f_V$  suggests that  $P_0 \approx 0$ , and the total distribution,  $P_0 - P_5$ , is 0:09:28:41:19:03 with  $\langle f_V \rangle = 0.32$  for H + Cl<sub>2</sub>O. This distribution is in fortuitous agreement with a first generation, measured relaxation result, <sup>17(a)</sup>  $P_1 - P_5 = 11:33:37:15:04$ . In the early work using an integrating sphere reactor and a PbS detector, <sup>17(a)</sup> emission from HOCI

Expt.	[H <sub>2</sub> ] <sup>a</sup> (10 <sup>12</sup> m	[RCl] <sup>a</sup> olecule cm <sup>-3</sup> )	$\Delta t$ (ms)	<b>P</b> <sub>1</sub>	<b>P</b> <sub>2</sub>	<i>P</i> <sub>3</sub>	<i>P</i> <sub>4</sub>	P <sub>5</sub>	P <sub>6</sub>
Cl <sub>2</sub> -1	5.3	1.8-3.9	0.15	12	39	40	9		
$Cl_2 - 2$	5.3	1.4-2.8	0.15	12	40	39	9	•••	•••
$Cl_2^-3$	37.0	1.0-5.0	0.15	16	42	35	7	•••	•••
$Cl_2^-4$	10.3	2.0-6.1	0.11	13	39	38	10	•••	•••
Cl <sub>2</sub> -5	13.5	3.4-13.6	0.11	11	40	40	9	•••	•••
Cl <sub>2</sub> -6	12.5	5.4-15.3	0.11	14	37	39	10	•••	•••
C1,-7	12.7	4.7-10.0	0.11	13	40	40	7	•••	•••
Cl8	12.5	1.4-7.9	0.11	12	40	41	7	•••	•••
Cl <sub>2</sub> -9	12.0	3.5-11.0	0.11	11	40	40	9	•••	
-	Nascent	t distribution (FR	0	12	38	40	10	•••	
	Nascent	t distribution (AR	J <sup>b</sup>	14	40	40	5	•••	
Cl <sub>2</sub> O-1	5.3	1.2-3.4	0.15	09	28	41	19	03	
Cl <sub>2</sub> O-2	22.0	1.4-3.1	0.15	09	31	40	17	02	
CI-O-3	35.0	3.3	0.15	10	32	39	16	02	
C1,0-4°	3.5	1.6	0.35	12	31	38	17	02	•••
CINO-1°	3.5	1.1-4.4	0.24	06	09	19	29	24	13

TABLE II. HCl(v) distributions for the  $Cl_2$ ,  $Cl_2O$ , and NOCl reactions.

<sup>a</sup> [H<sub>2</sub>] and [RCl] were varied within the range indicated.

<sup>b</sup> From extensive AR experiments in Ref. 8.

<sup>c</sup>Experiments from the larger diameter flow reactor, Ref. 9(b).

was also observed with a  $I_{\rm HOCl}$  / $I_{\rm HCl}$  ratio of 1/90. In the present work HOCl<sup>†</sup> was never observed and HOCl must be a very minor channel or possibly it arises from stabilization of H + ClO by collisions with the walls of the reactor.

The ClNO reaction was studied only in the larger reactor. One experiment is included in Table II with  $[H_2] = 3.5 \times 10^{12}$  molecule cm<sup>-3</sup> and [ClNO] = 1.1 to  $4.0 \times 10^{12}$  molecule cm<sup>-3</sup>; the  $P_V$  were independent of [ClNO]. The emission from HCl(v = 7) was not observed and the average distribution was  $P_1 - P_6$ 



FIG. 2. Plot of  $P_{\nu}$  (HCl) vs [Cl<sub>2</sub>O] for experiment Cl<sub>2</sub>O-1 of Table II. For these experiments [H<sub>2</sub>] was  $5.3 \times 10^{12}$  molecule cm<sup>-3</sup>. The average  $P_{\nu}$  values were assigned as 9:28:41:19:3.

= 06:09:19:29:24:13. This distribution agrees with that reported by Berquist *et al.*<sup>20</sup> from low resolution spectra in a flow reactor,  $P_1-P_7 = 04:07:15:26:29:15:04$ , as well as AR data,<sup>18</sup>  $P_3-P_7 = 24:29:30:14:03$ . The AR study provides information about the rotational excitation and  $\langle f_R \rangle \approx 0.07$ . Consideration of all three studies suggests  $P_0-P_7 = 00:05:09:19:27:24:13:03$  as the nascent distribution and  $\langle f_V \rangle = 0.5$ .

#### C. $HF(\nu)$ distributions from CF<sub>3</sub>OF and F<sub>2</sub>O

Since these reactions are about three orders of magnitude slower than the Cl<sub>2</sub>O or ClNO reactions, high concentrations and longer times were needed to observe HF(v)emission. The HF(v) rotational distributions were 300 K Boltzmann for both F<sub>2</sub>O and CF<sub>3</sub>OF, in spite of their large exoergicities. Experiments with CF<sub>3</sub>OF were done with  $[H_2] = 1.6 \times 10^{12}$  and  $5.7 \times 10^{12}$  molecule cm<sup>-3</sup> with variable [CF<sub>3</sub>OF]. Although there was no dependence of the HF(v) distribution on [CF<sub>3</sub>OF] up to  $\leq 9.0 \times 10^{13}$  molecule cm $^{-3}$ , the distributions for the two [H<sub>2</sub>] were different;  $P_1 - P_7 = 08:14:22:27:18:09:02$  and 16:19:23:25:13:04:01 for the lower and higher [H<sub>2</sub>], respectively. A secondary reaction with  $CF_3O$ , which would give HF in low v levels by an elimination mechanisms, may be responsible for the larger population in lower levels for the experiment with higher  $[H_2]$ . We favor the distribution obtained with the lower  $[H_2]$  as the best estimate of the nascent distribution and  $\langle f_{\nu}(\text{HF}) \rangle$  is 0.39.

Only one experiment was done with OF<sub>2</sub> because of its highly oxidizing nature. The [H<sub>2</sub>] was  $5.7 \times 10^{12}$  molecule cm<sup>-3</sup> and the [F<sub>2</sub>O] was increased up to  $4.0 \times 10^{13}$  molecule cm<sup>-3</sup>. The HF(v) distribution,  $P_1-P_7$ = 12:17:18:18:18:13:04, showed no dependence on [F<sub>2</sub>O]. If, as in case of CF<sub>3</sub>OF, the vibrational distribution has a component from a secondary reaction, the nascent distribution may be somewhat more sharply peaked in v = 4-6. This distribution is an improvement over a very early study<sup>17(c)</sup>; however, trace emission from v = 8 was observed before when the HF( $\Delta v = 2$ ) emission was monitored. Nevertheless, the reaction does not give significant population in the highest allowed levels, v = 8-10, and  $\langle f_V \rangle$  is ~0.38.

#### D. OH(v) distributions from NO<sub>2</sub> and ClO<sub>2</sub>

The NO<sub>2</sub> and ClO<sub>2</sub> experiments are listed in Table III and a typical OH( $\Delta v = 1$ ) emission spectrum from the ClO<sub>2</sub> reaction is shown in Fig. 3. The spin-orbit state distributions were Boltzmann with  $OH(^{2}\Pi_{3/2})/OH(^{2}\Pi_{1/2}) = 2.0$ . A new finding, relative to our earlier FR work,<sup>10</sup> was a small non-Boltzmann component to the rotational distributions for pressures below 0.4 Torr for both the  $NO_2$  and  $ClO_2$ reactions, see Fig. 3. The recommended OH(v) nascent distribution  $(P_0 - P_3 = 44:31:19:06)$  from NO<sub>2</sub><sup>8</sup> serves as a benchmark. The observed distribution from NO2 was invariant for  $[NO_2] \leq 8 \times 10^{12}$  and  $[H_2] \leq 30 \times 10^{12}$  molecules cm<sup>-3</sup>, and the distributions for the  $A_{u,J}$  values of LWR and Mies were  $P_1: P_2: P_3 = 60:36:04$  and 57:39:04, respectively, see Table III. The NO<sub>2</sub>-3 experiment at 0.35 Torr, showed a small high J envelope ( $J \ge 10.5$ ). The highest observed OH( ${}^{2}\Pi_{3/2}$ ) level was J = 16.5(N = 15); the fraction of the OH(v = 1) population in the high J component was 0.065. Our OH(v) distribution agrees with the accepted distribution  $(P_1 - P_3 = 56:34:10)$ ,<sup>8</sup> except that our  $P_3$  was always about 1/2 of that reported in AR measurements. We observed no systematic change in  $P_3/P_2$  with  $[H_2]$  or [NO<sub>2</sub>], and the difference in the AR and FR experiments presumably arises because of the weak v = 3 signal in both experiments. Klenerman and Smith<sup>15</sup> also reported a lower  $P_3$  value in their IRCl studies using a SISAM spectrometer; however, their  $P_2$  value also is low and vibrational relaxation may not have been fully arrested.

The NO ( $\Delta v = 1$ ) emission from v = 1 and 2 was observed from  $H + NO_2$ . Our new spectrum<sup>9(a)</sup> closely resembles the one shown in Ref. 10 and it is not included here. Due to the sharp decline of the detector response below 1870 cm<sup>-1</sup>, the P branch lines for v = 1 and 2 and the R branch lines (J < 5.5) for v = 2 were very weak. The relative  $N_{v,J}$ populations were calculated from the R branch line intensities, using the  $A_{v'J'}^{v'J'}$  values from the thermally averaged<sup>34</sup>  $A_{v'}^{v'}$  ( $A_0^1 = 10.78$  and  $A_1^2 = 20.43 \text{ s}^{-1}$ ) and calculated line strength factors<sup>35</sup> A plot of  $\ln\{I_{J'}/S_{J'J'}\}$  vs  $\{J'(J'+1)\}$ was constructed<sup>9(a)</sup> to check the validity of the data reduction; the plot gave a rotational temperature of  $260 \pm 20$  K. The v = 1 and 2 relative population was  $P_1:P_2 = 70:30$ . Assuming  $P_0 \approx P_1$  the distribution becomes  $P_0 - P_2 = 41:41:18$ which corresponds to  $\langle f_V(NO) \rangle = 0.13$ . After adjusting for the response function, the [OH(v = 1)]/[NO(v = 1)]ratio was  $\approx 1.1$ .

Figure 4 shows a plot of  $P_{\nu}$  vs  $[ClO_2]$  for  $[H_2] = 13.5 \times 10^{12}$  molecule cm<sup>-3</sup>; the distribution was invariant for  $[ClO_2] \leq 9.0 \times 10^{12}$  molecule cm<sup>-3</sup>. The dependence of the OH(v) distribution upon [H] is shown in Fig. 5. There is a systematic trend with  $P_1$  and  $P_2$  increasing at the expense of  $P_4$  for larger  $[H_2]$ . However, for  $[H_2] \leq 2 \times 10^{13}$ 

TABLE III. OH(v) distributions for the  $ClO_2$  and  $NO_2$  reactions.

 $(10^{12} \text{ molecule cm}^{-3})$ 

[Reagent]

1.7-2.5

1.8-9.0

2.1 - 3.1

2.6-9.6

2.1 - 5.1

3.1

 $\Delta t$ 

(ms)

0.15

0.11

0.11

0.11

0.11

0.11

 $P_1$ 

20

23

15

18

17

20

15

18

16

18

20ª

22ª

 $P_2$ 

27

28

27

28

24

26

25

27

25

27

24

26

 $P_3$ 

27

27

28

28

27

27

28

28

27

27

26

26

 $P_4$ 

26

22

30

26

32

27

31

26

32

28

30

26

Comments

A<sub>Mics</sub>

A<sub>LWR</sub>

 $A_{\rm Mies}$ 

ALWR

A<sub>Mies</sub>

ALWR

A<sub>Mies</sub>

ALWR

 $A_{\rm Mies}$ 

 $A_{\rm LWR}$  $A_{\rm Mies}$ 

ALWR

[H<sub>2</sub>]

5.3

13.5

20.0

12.5

10.2

5.0-59.0

Experiment

ClO<sub>2</sub>-1

ClO<sub>2</sub>-2

ClO<sub>2</sub>-3

ClO<sub>2</sub>-4

ClO<sub>2</sub>-5

ClO<sub>2</sub>-6\*

	Nascent d	istribution		19	28	28	25	$A_{\rm LWR}$	
NO <sub>2</sub> -1	12.0	2.5-7.7	0.11	57	39	04		A <sub>Mies</sub>	
				59	37	04		ALWR	
NO₂-2	12.5	1.7-5.1	0.11	58	37	05		A <sub>Mies</sub>	
				60	36	04		$A_{\rm LWR}$	
NO <sub>2</sub> -3 <sup>b,c</sup>	30.0	4.0	0.11	61 <sup>6</sup>	35	04		A <sub>Mics</sub>	
				63 <sup>ь</sup>	33	04		$A_{\rm LWR}$	
	Nascent d	istribution		60	36	04		$A_{\rm LWR}$	
*The fraction		n in the high I le	vels was (		0.045	for this a	vnerim	mt at 0.4 To	

<sup>a</sup> The fractional population in the high J levels was 0.11 and 0.045 for this experiment at 0.4 Torr and  $[H_2] = 2 \times 10$  molecule cm<sup>-3</sup>. The entry for the vibrational distribution in the table is for the low  $[H_2]$  range.

<sup>b</sup> The fractional population in high J levels for v = 1 was 0.064.

<sup>c</sup> The NO(v) distribution from this experiment was determined as  $P_1/P_2 = 70:30$ .



FIG. 3. The OH( $\Delta v = 1$ ) spectrum from the H + ClO<sub>2</sub> reaction for [H<sub>2</sub>] =  $3.0 \times 10^{13}$  and [ClO<sub>2</sub>] =  $4.0 \times 10^{12}$  molecule cm<sup>-3</sup> at 0.35 Torr. The *R* branch emission lines from several *J* levels are identified to aid in the overall assignments.



FIG. 4. Plot of  $P_{V}(OH)$  vs [ClO<sub>2</sub>] for the ClO<sub>2</sub>-2 experiment in Table III. The [H<sub>2</sub>] was  $13.5 \times 10^{12}$  molecule cm<sup>-3</sup>. The  $P_{V}$  were independent of [ClO<sub>2</sub>], and average values were assigned as  $P_{1}(\Box):P_{2}(\blacksquare):P_{3}(\bigcirc):P_{4}(\textcircled{O}) = 18:28:28:26$ .

molecule cm<sup>3</sup> the distribution is nearly constant. This conclusion is confirmed by experiments ClO<sub>2</sub>-2 through ClO<sub>2</sub>-5, which give the same distributions for different  $[H_2]$ . The nascent distribution given in Table III is based on the average from experiments with 0.11 ms reaction time. The dependence of the OH(v) distribution on  $[H_2]$  demonstrates that the secondary reaction, H + ClO, is responsible for the change in OH(v) distribution in Fig. 5. For the Mies'  $A_{v,I}$ values,  $P_1 - P_4 = 15 \pm 1.927 \pm 0.828 \pm 0.830 \pm 1.0$ , and for the LWR values  $P_1 - P_4 = 19 \pm 1.1:28 \pm 0.8:28 \pm 0.8:25$  $\pm$  1.0. The distributions obtained from the two sets of  $A_{n,I}$ values do not differ significantly, although  $P_1$  is higher and  $P_4$  is little lower for the LWR Einstein coefficients. The present study gives a slightly improved distribution relative to our earlier report,  ${}^{10}P_1 - P_4 = 20:25:27:28$ , for Mies'  $A_{v,J}$  values.

In addition to the 300 K Boltzmann envelope, the OH(v = 1 and 2) rotational distributions from H + ClO<sub>2</sub> had small high J ( $\geq 10.5$ ) envelopes. The highest observed levels for OH( ${}^{2}\Pi_{3/2}$ ) were 22.5(N = 21) and 19.5(N = 18) with high J components of 0.11, and 0.045 for v = 1, and 2, respectively. These rotational distributions will be combined with LIF data<sup>13(a)</sup> to estimate the nascent rotational distribution in Sec. IV. The vibrational surprisal plot, Fig. 6, is linear for a three-body prior, for a prior that includes the rotations of ClO, and for the full four-body prior. Since LIF studies gave  $N_0 / N_1 = 0.7 \pm 0.2^{13(a)}$ , we selected a ratio of 0.6 and the distribution based on the  $A_{v,J}$  values of LWR is  $P_0-P_4 = 10:17:25:25:23$  with  $\langle f_V(OH) \rangle = 0.51$ .



FIG. 5. Plot of  $P_{\nu}(OH)$  vs  $[H_2]$  for the H + ClO<sub>2</sub> reaction. The [ClO<sub>2</sub>] was  $3.1 \times 10^{12}$  molecule cm<sup>-3</sup>. The  $P_{\nu}(OH)$  become dependent on [H<sub>2</sub>] for concentrations above  $\sim 20 \times 10^{12}$ molecule cm<sup>3</sup>.

# E. HX (X=CI,F,C) formation rate constants

The HX formation rate constant,  $k_f$ , for a given reaction can be obtained by comparing the [HX] from the reaction under consideration to a reference reaction for conditions that follow the differential rate law:

$$[\mathbf{HX}] = k_f [\mathbf{H}] [\text{reagent}] \Delta t. \tag{1}$$

The [HCl] from NOCl and Cl<sub>2</sub>O, [HF] from CF<sub>3</sub>OF and F<sub>2</sub>O, and [OH] from ClO and NO<sub>2</sub> were compared to [HCl] from  $H + Cl_2$  by doing pairwise experiments for each reactant under identical conditions. Since the populations of the two OH spin-orbit states were Boltzmann, the

 $[OH(^{2}\Pi_{3/2})]$  determined from the spectra was scaled by a factor of 1.5 to account for the  $[OH(^{2}\Pi_{1/2})]$ . The contribution from the H<sup>37</sup>Cl isotope was taken into account for [HCl]. Plots of [HX(v>1)] vs [reagent] for Cl<sub>2</sub>O, NO<sub>2</sub>, and ClO<sub>2</sub> are shown in Fig. 7. Linear plots were found for [reagent] $\leq 2.0 \times 10^{13}$  molecule cm<sup>-3</sup>, and the slopes give the relative rate constants. Some experiments were done with constant  $[ClO_2]$  and variable [H]; the [OH] increased linearly for  $[H_2] \leq 2 \times 10^{13}$  molecule cm<sup>-3</sup> in accord with reaction (1). Table IV gives a summary of the HX(v>1) formation rate constants. The absolute rate constants for the HX(v>0) formation were calculated using the  $P_0$  values



FIG. 6. The  $P_V(OH)$  vs  $f_V$  and vibrational surprisal plots for the  $H + ClO_2$  reaction. The surprisal plots are for a three-body prior,  $\Box$ , and a prior,  $\bullet$ , that included the rotations of ClO; the  $\lambda_V$  (and predicted  $P_0 / P_1$ ) values for the two priors are -4.0(0.53) and -8.0(0.27). For the full four-body prior, not shown,  $\lambda_V = -10.0$  and  $P_0 / P_1 = 0.2$ .



FIG. 7. Plots of relative [HX(v>1)] vs reagent concentration the Cl<sub>2</sub>O, ClO<sub>2</sub>, NO<sub>2</sub>, and Cl<sub>2</sub> reactions. Each reaction was studied pairwise with the Cl<sub>2</sub> reaction for  $[H_2] = 1.35 \times 10^{13}$  molecule cm<sup>-3</sup>. The  $A_{u,f}$ (OH) values of LWR were used to obtain [OH].

cited in the previous section and the 300 K rate constant for the Cl<sub>2</sub> reaction,  $2.06 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>. A direct comparison was made between CF<sub>3</sub>OF and F<sub>2</sub>O under identical conditions.<sup>9(b)</sup> The ratio was 1.5 in favor of CF<sub>3</sub>OF, which supports the rate constant measured vs Cl<sub>2</sub>.

For most  $ClO_2$  experiments, the  $Cl_2$  and  $ClO_2$  were simultaneously added to the reactor to eliminate possible uncertainty due to fluctuations in the conditions. In one experiment the reagents were added separately to confirm that there was no artifact due to mixing. The average  $OH(v \ge 1)$ rate constant from five measurements, relative to  $k_{CL}$ , is  $3.0 \pm 0.3$ . Including  $P_0$  gives the total rate constant as  $(6.9 \pm 0.7) \times 10^{-11}$  and  $(7.8 \pm 0.8) \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup> for the Einstein coefficients of Mies and LWR, respectively. The ratio of the rate constants for NO<sub>2</sub> to ClO<sub>2</sub>, each measured relative to  $H + Cl_2$ , is 1.7, and 1.9, for the  $A_{n,J}$  values of Mies and LWR, respectively. Direct comparisons of the  $OH(v \ge 1)$  formation rate constant from NO<sub>2</sub> and ClO<sub>2</sub> also were made. The ratio was  $1.14 \pm 0.20$ , and  $1.27 \pm 0.25$  for the two sets of  $A_{v,J}$  (OH) values, including the  $P_0$  contributions gives  $k_{NO_2}$  {OH( $v \ge 0$ )}/ $k_{CO_2}$  {OH( $v \ge 0$ )} as 1.9 ± 0.4 and  $2.1 \pm 0.4$ .

The reliability of the  $A_{\nu,J}$  (OH) values can be checked by comparing our OH formation rate constant from NO<sub>2</sub> to the independently measured total rate constant. Two separate rate constants measurements were done for NO<sub>2</sub> (Table IV). The average of the two experiments for OH( $\nu \ge 0$ ) was  $(11.9 \pm 1.0) \times 10^{-11}$  and  $(14.9 \pm 1.3) \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup> for the  $A_{\nu,J}$  (OH) values of Mies and LWR, respectively. The literature values for the NO<sub>2</sub> rate constant range from  $(11.0 \pm 3.0) \times 10^{-11}$  to  $(14.1 \pm 2.6) \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>. The most recent<sup>39</sup> measurement, which is the latter value, was obtained from flash-photolysis and discharge flow measurments in the same laboratory. The previous three measurements<sup>36,38</sup> were based on the flow reactor method. The uncertainty in all these measurements was  $\approx 20\%$ , but

TABLE IV. 300 K rate constants.

<b>Reaction</b>	Rel. [HX(v>1)]*	Abs. $[HX(v>0)]$ (10 <sup>-11</sup> cm <sup>3</sup> s <sup>-1</sup> )	Literature	Comments
$H + Cl_2$	1.0	2.06	·······	37(a),37(b)
H + NOCI	0.95 ± 0.4	$(1.96 \pm 0.82)$		9(b)
			$(1.82 \pm 0.27)$	37(c)
$H + Cl_2O$	(2.0 ± 0.4) <sup>b</sup>	$(4.1 \pm 0.8)$	—	this work
_	$(3.1 \pm 0.7)$	$(6.4 \pm 1.5)$		9(b)
$H + F_2O$	$(0.68 \pm 0.4)^{b} \times 10^{-3}$	$(1.5 \pm 0.8) \times 10^{-3}$		9(b)
$H + CF_3OF$	$(1.5 \pm 0.2)^{b} \times 10^{-3}$	$(3.2 \pm 0.4) \times 10^{-3}$		9(b)
$H + NO_2^{c,d}$	$3.1 \pm 0.36$	$(11.9 \pm 1.0)$		AMies
-	3.9 + 0.3	(14.9 + 1.3)		Arwa
	<del></del>		11.0 + 3.0	36
			$13.2 \pm 1.8$	38(a)
			$12.8 \pm 2.5$	38(b)
			14.1 + 2.6	39
$H + ClO_3^d$	3.0 + 0.3	(6.9 + 0.7)	- ··· T -···	Aren
• - 2	3.4 + 0.3	$(7.8 \pm 0.8)$		Arm
		(,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	5.7 ± 1.2	40

<sup>a</sup> In converting to absolute rate constants  $k_{Cl_2} = 2.06 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  was used; the HCl(v) distribution was  $P_0 - P_4 = 0.12:38:40:10$ .

<sup>o</sup> The relative NO<sub>2</sub> rate constant measured directly vs ClO<sub>2</sub>, was found to be 1.9, and 2.1 for the Einstein coefficients of Mies and LWR, respectively.

<sup>d</sup> The comparisons for NO<sub>2</sub> and  $ClO_2$  are based upon 2 and 5 comparison plots, respectively, such as shown in Fig. 7.

<sup>&</sup>lt;sup>b</sup> These results are based upon a single comparison plot such as shown in Fig. 7.

three<sup>38,39</sup> of the four measurements gave  $k_{\text{NO}_2} \ge 13.0 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup> in agreement with our rate constant,  $14.9 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup> based upon the LWR set of  $A_{v,J}$  (OH). The rate constant derived from the  $A_{vJ}$  values of Mies, although within the experimental uncertainty, seems low by ~20%.

### F. The CIO reaction

To observe secondary reactions the [H] must be increased. For  $[H_2] \leq 3.0 \times 10^{13}$ , [reagent]  $\leq 1.0 \times 10^{13}$  molecule cm<sup>-3</sup> and  $\Delta t \le 0.15$  ms, the HCl(v) and OH(v) distributions from  $Cl_2$  and  $NO_2$  were not significantly affected by relaxation and the primary product concentrations still had a first order dependence on  $[H_2]$  and [reagent]. Since the vibrational relaxation rate constants for H atoms<sup>41</sup> are large, the major factor in vibrational relaxation is expected to be the [H]. The onset of vibrational relaxation and OH removal can be expected for  $[H_2] > 3.0 \times 10^{13}$  molecule cm<sup>-3</sup> at  $\Delta t = 0.15$  ms. For example, with  $[H_2] = 4.1 \times 10^{13}$  and  $9.2 \times 10^{13}$  molecule cm<sup>-3</sup> for  $\Delta t = 0.4$  ms the Cl<sub>2</sub> reaction gave  $P_1 - P_4$  of 21:40:33:06 and 23:40:31:06, respectively, vs the nascent distribution of 12:38:40:10. In a similar way increasing  $[H_2]$  to  $3.0 \times 10^{13}$  molecule cm<sup>-3</sup> for the NO<sub>2</sub> reaction gave  $P_1 - P_3 = 64:33:03$  vs the nascent distribution of 60:36:04. These observations are helpful in understanding results for the ClO reaction studied as a secondary step in the Cl<sub>2</sub>O and ClO<sub>2</sub> systems.

#### 1. The HCl channel

Preliminary experiments were done for  $\Delta t = 0.45$  ms  $[H_2] = 1.6 \times 10^{13}$  molecule cm<sup>-3</sup> with  $[ClO_2]$  varied from 3.1 to  $8.4 \times 10^{12}$  molecule cm<sup>-3</sup>, see Table V. The OH(v) distribution was  $P_1 - P_4 = 28:28:24:19$  and the HCl(v) distribution was  $P_1 - P_4 = 43:32:16:07$ ; the  $P_v$  (OH) did not show any dependence on  $[ClO_2]$ , but the HCl(v) changed slightly with  $[ClO_2]$ . The increase in the OH(v = 1) populations, compared with the nascent distribution (19:28:28:25), indicates relaxation and/or a contribution due to the secondary reaction. Experiments were attempted for shorter reaction time ( $\Delta t = 0.2$  ms) and the same  $[H_2]$ ; although, the HCl(v) emission could be detected, the poor S/N ratio prevented assignment of a reliable HCl(v) distribution. For the

second set of experiments in Table V,  $[ClO_2]$  was  $8.5 \times 10^{12}$ and  $[H_2]$  ranged from  $1.3 \times 10^{13}$  to  $6.6 \times 10^{13}$  molecule cm<sup>-3</sup> with  $\Delta t = 0.2$  ms. The HCl(v) and OH(v) distributions show some dependence on  $[H_2]$ , and extrapolation to  $[H_2] = 0$  gave  $P_V(OH)$  as  $P_1-P_4 = 27:28:24:21$  and  $P_V$ (HCl) as  $P_1-P_4 = 37:29:21:13$ . A third experiment was done with  $[ClO_2] = 2.8 \times 10^{12}$  molecule cm<sup>-3</sup> and  $[H_2]$ was varied from 2.2 to  $4.4 \times 10^{13}$  molecule cm<sup>-3</sup>; the extrapolated distributions for OH and HCl were  $P_1-P_4$ = 27:29:24:20 and 36:33:19:12, respectively. These estimates for the HCl(v) distribution differ markedly from the narrow distributions from the Cl<sub>2</sub>, NOCl, and Cl<sub>2</sub>O reactions.

The  $[\Sigma_v OH]$  concentration did not show first order dependence on  $[H_2]$  for entries 2 and 3 of Table V, and the ClO rate constant can not be determined using the differential rate law. However, estimates for the OH(v) distribution, OH/HCl branching, and the rate constant were obtained as follows from the  $[H_2] = 2.7$  and  $2.2 \times 10^{13}$  molecule cm<sup>-3</sup> data. From the nascent distribution from the ClO<sub>2</sub> reaction and the observed [OH(v = 4)], the [OH(v = 1,2,3)] contribution from the ClO<sub>2</sub> reaction was calculated. The difference between the observed [OH(v)] and the calculated  $[OH(v)]_{ClO_{2}}$  gives the contribution of the ClO reaction from which the OH/HCl branching, the OH(v) distribution from the CIO reaction and the rate constant, using the expression<sup>4(b)</sup> [Sec]/[Pri] =  $k_{sec} \times [H] \times \Delta t/2$ , was estimated. The two sets of data gave the OH(v) distribution as  $P_1 - P_3 = 51:32:17$  and 51:35:14, the OH/HCl branching as 5.0 and 4.2, and  $k_{sec} \leq 2.5 \times 10^{-10}$  and  $\leq 2.0 \times 10^{-10}$  $cm^3 s^{-1}$ . These numbers are approximate because (i) the reaction conditions were not first order (  $\sim 50\%$  of ClO<sub>2</sub> was consumed during the reaction time of 0.2 ms) and (ii) the vibrational relaxation of OH(v) may have been significant or some of the OH(v) formed in the primary reaction could have been removed. These factors make the estimated  $k_{sec}$  an upper limit.

#### 2. The OH channel

Table VI summarizes the attempts to observe OH(v) from the H/Cl<sub>2</sub>O system. Since the Cl<sub>2</sub>O reaction is two

 $[ClO_2]$ OH(v) HCl(v)  $[H_2]$ P₄  $P_1$  $P_3$  $P_4$ Σ"ΟΗ  $\mathbf{P}_1$  $P_2$  $\mathbf{P}_3$  $\Sigma_{v}$ HCl  $P_2$ 47 15 06 1.6 0.84 28 30 23 15 31 0.59 28 29 25 18 42 33 17 08 28 0.31 27 24 21 43 32 17 08 24 1.3 0.85 28 28 21 127 could not be obs erved 2.7 31 23 17 42 29 163 30 17 10 12 4.8 34 29 22 15 179 48 32 12 07 16 35 6.6 29 22 15 187 50 32 12 07 20 2.8 17 2.2 31 30 22 67 30 42 16 10 5.9 3.3 35 30 21 14 76 51 29 11 10 8.3 4.4 35 31 20 14 74 48 27 14 10 8.6

TABLE V. The HCl(v) channel of the ClO reaction from the H/ClO<sub>2</sub> system.<sup>a,b</sup>

\*All concentrations are in units of 1013 molecule cm3.

<sup>b</sup> The  $\Delta t$  was 0.45 ms for the first experiment and 0.2 ms for the second and third set of experiments.

<b>[11]</b> )				НС	l(v)				OH	[(v)	
$(10^{13} \text{ molect})$	ule cm <sup><math>-3</math></sup> )	<i>P</i> <sub>1</sub>	<b>P</b> <sub>2</sub>	<i>P</i> <sub>3</sub>	P <sub>4</sub>	<i>P</i> <sub>5</sub>	Σ, ΗCl	<b>P</b> <sub>1</sub>	P <sub>2</sub>	<i>P</i> <sub>3</sub>	Σ"ΟΗ
12.4	1.3	46	31	17	05	01		54	46		
4.1	0.66	19	33	33	13	02	125	39	39	22	13
7.1		26	34	28	10	02	151	39	40	21	19
9.2	•••	28	35	26	09	02	153	40	40	20	21
11.2		30	35	25	08	02	165	41	38	20	24

TABLE VI. The OH channel of the ClO reaction from the H/Cl<sub>2</sub>O system.\*

<sup>a</sup> The reaction time for these experiments was 0.4 ms.

times slower than the  $ClO_2$  reaction and the  $A_{v,J}(OH)$  are three times smaller than  $A_{v,J}$  (HCl), rather extreme conditions were necessary to observe the OH product. A reaction time of 0.4 ms was selected by using a movable reagent inlet. The [H<sub>2</sub>] and [Cl<sub>2</sub>O] were  $12 \times 10^{13}$  and  $1.3 \times 10^{13}$ molecule  $cm^{-3}$ , respectively, in the first experiment. The OH(v) distribution was  $P_1 - P_2 = 54:46$  and the HCl(v) distribution was  $P_1 - P_5 = 46:31:17:05:01$ . The second experiment was done with variable  $[H_2]$  in anticipation of extrapolating to zero [H]. The OH(v) distribution showed very little dependence upon  $[H_2]$  in this range, which must be fortuitous considering that OH(v) relaxation by H atoms is more facile than HCl(v) relaxation. The extrapolated OH distribution,  $P_1 - P_3$ , was 40:40:20 with an uncertainty of 20%. These data imply that the OH(v) distribution from the ClO reaction is rather flat.

# **IV. DISCUSSION**

# A. Reliability of the vibrational distributions and rate constants

The energy disposal for the reactions studied is summarized in Table VII. The vibrational distributions for  $NO_2(P_1 -$ 

$P_3 = 60:36:04$ ) and $Cl_2(P_1 - P_4 = 12:38:40:10)$ reactions
agree with the previously accepted distributions for these
reactions (56:34:10 and 14:40:40:05). The HCl(v) distribu-
tion from Cl <sub>2</sub> was not affected by the new $A_{v,J}$ (HCl). <sup>21(b)</sup>
The $OH(v)$ distribution from NO <sub>2</sub> calculated from the two
sets of $A_{v,J}(OH)$ did not differ significantly, however, we
prefer the distribution from the LWR values. The absence of
HX(X = Cl,O) vibrational relaxation and the linear de-
pendence of the [product] on [RX] and [H] for each reac-
tion was verified. Therefore, the nascent vibrational distri-
butions should be reliable. Our only reservation is for
CF <sub>3</sub> OF and OF <sub>2</sub> , because relatively high [H] was required.
For these cases, the $\langle f_V(\text{HF}) \rangle$ values, ~0.39, could be low-
er limits because of small contributions to $HF(low v)$ from
secondary reactions $(H + OF \text{ and } OCF_3)$ . However, this
effect should be small, especially for $CF_3OF$ .

Uncertainties in the rate constants for product formation arise from (1) the reagent concentration measurements ( $\leq 5\%$ ) and (2) the assignment of [HX] from the relative intensities ( $\leq 10\%$ ). Together these contribute to  $\approx 20\%$ uncertainty in the rate constants. The ClNO rate constant,  $1.96 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>, compares well with an independent measurement<sup>37(c)</sup> based upon loss of [H]. The uncertainty

Reaction $\langle E \rangle$ (kcal mol <sup>-1</sup> )		Vibration distribution									
	$P_0$	<i>P</i> <sub>1</sub>	<b>P</b> <sub>2</sub>	<i>P</i> <sub>3</sub>	P <sub>4</sub>	<i>P</i> <sub>5</sub>	P <sub>6</sub>	<b>P</b> <sub>7</sub>	$\langle f_V \rangle$	$\langle f_R \rangle$	Comments
Cl <sub>2</sub> 47.9	0	12	38	40	10				0.37	0.07	this work and Ref. 8
Cl <sub>2</sub> 0 71.6	0	9	28	41	19	3			0.32	≤0.05	this work
CINO 67.7	0	5	9	19	27	24	13	3ª	0.50	~0.07ª	
NO <sub>2</sub>	44	33	20	03					0.25	0.22 <sup>b</sup>	this work
ClO <sub>2</sub>	10	17	25	25	23	•••	0.51	~0.16 <sup>c</sup>	this we	ork	
ClO <sup>d</sup>		40	40	20					≥0.40 <sup>d</sup>		OH channel
39.7		36	31	20	13				≥0.31 <sup>d</sup>		HCl channel this work

\* This distribution is an average from this work plus results of Refs. 18 and 20; The  $\langle f_R \rangle$  is from Ref. 18.

<sup>b</sup> The  $\langle f_R \rangle$  was taken from Ref. 18.

<sup>c</sup> The  $\langle f_R \rangle$  was determined from the rotational distribution given in Ref. 13(a) for v = 0 and 1; see the text for details.

<sup>d</sup> These data provide lower limits for  $\langle f_{V}(\text{HCl}) \rangle$  and  $\langle f_{V}(\text{OH}) \rangle$ , see Ref. 16 for more definitive work;  $P_{0}$  was assumed to be the same as  $P_{1}$  for this calculation.

TABLE VII. Summary of energy disposal.

for the  $CF_3OF$  and  $OF_2$  may be higher than 20%, due to the difficulty of quantitative gas handling for these reagents.

The OH formation rate constants for the ClO<sub>2</sub> and NO<sub>2</sub> reactions merit a few comments. The  $A_{n,J}$  (HCl) based upon an improved dipole moment function by Ogilvie<sup>21(b)</sup> are about 20% larger than than the older ones.<sup>21(a)</sup> In our previous work<sup>10</sup> we had recommended the  $A_{\mu}$  (OH) values that were based on the dipole moment function of Meyer and Rosmus.<sup>23(a)</sup> Subsequently, Rosmus et al. modified their dipole moment function.<sup>23(b)</sup> Langhoff et al.<sup>24</sup> have calculated  $A_{n,I}$  values using the latest dipole moment function of Ros $mus^{23(c)}$ ; the revised  $A_v$  values are 1.09, 1.07, and 1.03 times greater than the ones which we had calculated  $^{10}$  for v = 1,2, and 3, respectively. The NO<sub>2</sub> rate constant using the LWR set was  $14.9 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>, which is in excellent agreement with the most recent rate constant measurement<sup>39</sup>, The  $(14.1 + 2.6) \times 10^{-11}$  $cm^{3} s^{-1}$ . rate constant,  $11.9 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>, calculated using the  $A_{\mu I}$  (OH) of Mies, although within the experimental uncertainty, is somewhat low, and we recommend  $A_{n,I}$  (OH) of LWR. The  $ClO_2$  rate constant for either set of  $A_{v,J}(OH)$  is 30% higher than the single reported value in the literature.<sup>40</sup>

# B. OH rotational distributions from NO<sub>2</sub> and ClO<sub>2</sub>

Observation of emission from  $HF(J \ge 9)$  for reactions that produce high rotational states is quite common in the flow reactor using Ar carrier gas.<sup>2,4(b)</sup> Although the exponential gap law for R-T energy transfer is not exact,<sup>42</sup> higher rotational states certainly relax much more slowly than the mid or low J levels, which reach a 300 K Boltzmann population within our observation time ( $\Delta t \leq 0.15$  ms). Since the rotational constant of OH is very similar to that for HF, the rotational relaxation of high J states of OH should be arrested to some degree. The nascent OH(v = 1, J) distribution<sup>8(a)</sup> from  $H + NO_2$  is comparable to the HF(v = 1, J) distribution from  $F + H_2S$ ,<sup>4(b)</sup> and comparison of the steady-state distributions permits an estimate for the difference in rotational relaxation rates. The HF(v = 1) high J fraction was 0.35 from the H<sub>2</sub>S reaction<sup>4(b)</sup> at 0.5 Torr and 0.08 ms reaction time ( $P \times \Delta t = 0.04$  Torr ms) and it was 0.39 for 0.1 Torr and 0.14 ms reaction time ( $P \times \Delta t = 0.014$ ). For the  $NO_2$  reaction, the fraction was only 0.06 for 0.35 Torr and 0.15 ms reaction time ( $P \times \Delta t = 0.05$ ). The product of the Ar pressure and the reaction time is a measure of the number of collisions before  $HX_{v,J}$  is observed. If the data for  $H_2S$  are extrapolated to  $P \times \Delta t = 0.05$ , the high J fraction would be  $\approx$ 0.33, which suggests that the R-T relaxation rates of  $OH(J \ge 9)$  are about five times larger than that for **HF**(*J*≥9).

The nascent rotational distributions from  $\text{ClO}_2$  was estimated by combining our observation of the highest J level with the distribution reported in Ref. 13(a) for v = 0 and 1 (the rotational surprisal parameter,  $\theta_R$  was given as -4.0 for both v = 0 and 1). Our distributions extend to higher J levels, but still not to the thermochemical limit. Our highest observed levels for v = 1 and 2, shown in Fig. 8, were combined with  $\theta_R = -4.0$  to obtain the distributions for v = 1

FIG. 8. The OH rotational distributions from the ClO<sub>2</sub> reaction; O—FR data, •—calculated distributions. The calculated (nascent) rotational distributions were obtained using the prior distribution, given below with  $\theta_R = -4.0$  from Ref. 13(a).  $P^{\circ}(v,J;E) = (2J + 1) \sum_{\nu(ClO)}^{\nu_{max}} {E - E_{\nu}} (OH) - E_{\nu}(ClO) - E_{J}(OH) \}^{3/2} / \rho(v;E)$ . All distributions are normalized to unity and are terminated at the highest J level observed in our study. The points for  $J \ge 12$  for the v = 2 distribution have been scaled by a factor of 2 to aid in presentation.

and 2. For v = 3 and 4 the  $\langle g_R \rangle$  values were taken to be the same (0.34) as for v = 1 and 2. With these assumptions,  $\langle f_R (OH) \rangle$  was estimated as 0.16, which probably is an upper limit. Although the rotational surprisal parameter has a larger negative value for ClO<sub>2</sub> than for NO<sub>2</sub>, the  $\langle f_R \rangle$  is smaller because the distributions do not extend to the thermochemical limit and because the vibrational distribution from ClO<sub>2</sub> favors higher levels, which have lower  $\langle E_R \rangle$ .

# C. Dynamics of the Cl<sub>2</sub>O,ClNO, $F_2O$ , and CF<sub>3</sub>OF reactions

Plots of  $P_V$  vs  $f_V$ , see Fig. 9, demonstrate the similarity of the vibrational distributions for this class of reactions, which also includes ClNO<sub>2</sub>.<sup>8</sup> The HCl(v) and HF(v) distributions are narrow with  $\langle f_V \rangle$  between 0.35 and 0.5, and the distributions do not extend to the thermochemical limit. In fact the highest level is usually below  $f_V = 0.7$ ; the HCl(v) distribution from Cl<sub>2</sub>O is especially sharply peaked at  $f_V$ = 0.3. All observed rotational distributions in the flow reactor were 300 K Boltzmann and there is no evidence for high rotational excitation in the AR data for ClNO<sub>2</sub> or ClNO; The AR data for ClNO give  $\langle f_R (HCl) \rangle = ~0.07$  and  $\langle f_R \rangle$ for Cl<sub>2</sub>O was estimated as  $\leq 0.05$  by noting that  $\langle E_R \rangle$  must be similar or less than that for Cl<sub>2</sub>. If  $\langle E_R \rangle$  was much larger,





FIG. 9. The  $P_{V}$  (HX) vs  $f_{V}$  plots for the Cl<sub>2</sub>, Cl<sub>2</sub>O, ClNO, and CF<sub>3</sub>OF reactions. The HCl(v) distribution from ClNO<sub>2</sub> ( $P_1$ - $P_6$  = 5:10:25:35:22:3) (Ref. 8) with  $\langle E \rangle$  = 72.7 kal mol<sup>-1</sup> and  $\langle f_{V} \rangle$  = 0.40 closely resembles the distribution from CF<sub>3</sub>OF, but it is somewhat more narrow.

emission from high J levels would have been observed.<sup>5,6</sup> All indications are that the NO,<sup>18</sup> OCl, or OF fragments do not aquire much internal energy and, by difference,  $\langle f_T \rangle$  must be large. The low  $\langle f_R(HX) \rangle$  and the narrow vibrational distributions result in *very* compressed and nearly vertical contour plots of the microscopic formation rate constants  $k_{wJ}$  plotted vs  $f_R$  and  $f_V$ , see Ref. 18 for an example. Without doubt, these reactions belong to the dynamical class for which the energy disposal is controlled by the motion of the light H atom on a repulsive surface.<sup>12</sup> However, specific aspects of the potential surfaces, especially in the exit channel, are important for each reaction<sup>1,8,43</sup> and lead to the small differences in the patterns displayed in Fig. 9. In the absence of computed potential surfaces, analogy will be made to the photodissociation model introduced by Herschbach.<sup>44</sup>

For collinear reaction of H with Cl<sub>2</sub>, three new  $\sigma$  orbitals are formed by mixing the 1s<sub>H</sub>,  $\sigma_{(X-X)}$  and  $\sigma^{*}_{(X-X)}$  orbitals. The new  $\sigma$  orbital (HOMO) containing one electron has Cl– Cl antibonding character and the repulsive part of the H–Cl– Cl surface resembles that for the Cl<sup>2</sup><sub>2</sub> ( $\pi^{*3}\sigma^{*1}$ ) state. Extending this model to the triatomic chloride and fluoride molecules that proceed by a direct mechanism is appealing, although quantitative photodissociation data are not available. For each reaction the H atom attack will be collinear with the X–R bond and the electron will enter a  $\sigma^*$  orbital with introduction of strong repulsion into the X-R bond. We will consider the ClNO and  $Cl_2O$  cases in more detail.

Photodissociation data do exist for ClNO. The absorption continuum extends from 200 to 600 nm and several transitions must be considered; however, ab initio calculations permit assignments with some confidence.45 The  $\sigma^*_{(N-Cl)}$  (8*a'*) and  $\pi^*(3a'')$  are the first two LUMOs, the  $1s_H$ orbital can have overlap with the  $\sigma^*_{(N-Cl)}$  antibonding orbital (8a') for end-on attack at the chlorine atom or with the  $\pi^*$ type orbital (3a'') for sideways attack perpendicular to the plane of the molecule. The most direct analogy seems to be with the  ${}^{3}A'$  excited state (6a') (8a') from (6a')<sup>2</sup> excitation in the 350 nm region.  $^{45-48}$  The  $^{3}A'$  state is repulsive and dissociates to NO( $^{2}\Pi$ ) and Cl( $^{2}P$ ) products; the pioneering work of Bush and Wilson<sup>47</sup> showed that  $\sim 70\%$  of the energy was released to translational motion. The major part of the remainder was predicted to be NO rotation energy, based on the impulsive model for photodissociation, and this has been confirmed.<sup>48</sup> Other photofragment studies of ClNO indicate that the energy disposal is wavelength dependent,<sup>46,48</sup> but for  $\lambda > 350$  nm all excited states are repulsive and vibrational excitation of the NO fragment is negligible. The energy disposal for H + ClNO is  $\langle f_V(\text{HC1}) \rangle = 0.5$ ,  $\langle f_R(\text{HC1}) \rangle$ = 0.07,  $\langle f_T \rangle = 0.30^{19}$  with  $\langle f_V(NO) \rangle$  inferred to be small from failure to observe the NO( $\Delta v = 1$ ) emission.<sup>9(b),18</sup> By difference,  $\langle f_R(NO) \rangle$  can be estimated as  $\approx 0.13$ . The energy disposal to NO and the overall pattern is consistent with the photodissociation data from the  ${}^{3}A'$  state. Direct measurement of the NO distribution from chemical reaction with comparison to photodissociation data could be fruitful.

The LUMO for Cl<sub>2</sub>O is the  $\sigma^*_{(Cl-O)}$  antibonding 8*a'* orbital and coplanar attack of the H atom on the Cl-O bond would have overlap between this orbital and the 1s<sub>H</sub> orbital. Neither theoretical nor empirical information about the electronic states of Cl<sub>2</sub>O seem to be available. From the generalized Walsh diagram, the lowest excited state must involve the transition from the nonbonding 7*a'* or 2*a''* orbital to the 8*a'* orbital, leading to Cl + ClO. The absorption spectrum shows a continuum extending from the 230 to 600 nm, which is similar to that of ClNO.

### D. Dynamics of the ClO<sub>2</sub> reaction

The OH vibrational distribution is broad, the surprisal is linear with  $\lambda_{V} = -4.0$  or -10 for the three- and fourbody priors, respectively, and  $\langle f_{V}(OH) \rangle$  is 0.51. Since  $\langle f_{R}(OH) \rangle$  was estimated as 0.16, about 34% of the available energy must be partitioned between  $\langle E_{T} \rangle$  and  $\langle E_{I}$ (ClO) $\rangle$ . The rotational excitation in v = 1 and 2 extended only up to  $g_{R} = 0.7$  The highest levels are  $N_{v=1} = 21$ , and  $N_{v=2} = 19$  and there may be an angular momentum constraint to formation of higher rotational states. The energy disposal pattern for the ClO<sub>2</sub> reaction resembles that for the NO<sub>2</sub> reaction, although  $\langle f_{V}(OH) \rangle$  is larger and  $\langle f_{R}(OH) \rangle$ is smaller.

The  $ClO_2$  reaction is expected to proceed via an H–O'– ClO intermediate. According to MO considerations, the H

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atom will approach perpendicular to the plane of the molecule so as to have maximum overlap with the half-filled, HOMO  $(\pi^*, 2b_1)$  orbital, which has electron density mainly on the Cl atom. Migration of H from Cl to O will be followed by dissociation of HO'ClO to HO + ClO. Internal rotation of H-O' around the O'-Cl bond, as well as the H-O'-ClO out-of-plane bending vibration, can generate OH angular momentum during dissociation.<sup>49</sup> Both of these mechanisms are currently the subject of intense discussion and separating the two dynamical effects is difficult.<sup>49</sup> If the O'-Cl bond breaks while the OH is rotating around it, the orbital containing the electron on the OH radical will tend to be aligned in the same directions as the internal rotational angular momentum vector. Thus, there could be some selectivity for the two sets of  $\lambda$ -doublet states of OH. However, out-of-plane bending vibration will tend to reduce the specificity. The experimental<sup>13(a)</sup> evidence shows that the symmetric  $(A')\lambda$ doublet<sup>50</sup> set of states is marginally favored over the A'' set  $(A'/A'' = 1.3 \pm 0.3)$ , suggesting that there is little selectivity for the orientation of the p-orbital relative to the plane of rotation of OH. This result provides a contrast with the NO<sub>2</sub> reaction, which strongly favors the A' set of  $\lambda$ -doublet states. The H-atom probably also attacks the central atom and then migrates to give HO'-NO. However, the half-filled HOMO of NO<sub>2</sub> is a *p*-type orbital  $(6a_1)$  located on the N atom Thus, the  $H + NO_2$  reaction begins with all atoms having a propensity to be in a common plane.

#### **V. CONCLUSIONS**

The reaction dynamics for  $H + Cl_2O$ , ClNO,  $OF_2$ , and CF<sub>3</sub>OF are typical of direct H-atom reactions and give modest  $\langle f_V(\mathrm{HX}) \rangle$ , small  $\langle f_R(\mathrm{HX}) \rangle$ , and large  $\langle f_T \rangle$ . Analogy to photodissociation dynamics for these molecules supports the expectation that the potential surfaces are strongly repulsive in the exit channel. In contrast to the  $H + SCl_2$  reaction,<sup>8</sup> the product distributions from  $OCl_2$  and  $OF_2$  give no indications of microscopic branching (migratory dynamics). The OH(v) formation rate constant for  $ClO_2$  was determined as  $(7.8 + 0.8) \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>; the OH(v) distribution was  $P_0 - P_4 = 10:17:25:25:23$  with  $\langle f_V \rangle = 0.51$ . The energy disposal resembles that from the NO<sub>2</sub> reaction, but OH receives a higher fraction of the vibrational energy and a lower fraction of the rotational energy. The reaction is thought to proceed via a bound intermediate, HO-ClO. Emission from  $OH(v, J \ge 10.5)$  was observed from the ClO<sub>2</sub> and NO<sub>2</sub> reactions at 0.35 Torr, along with the Boltzmann envelope of levels. Comparison with  $F + H_2S$ , which generates a similar nascent HF(v = 1, J) distribution, suggests that the rotational relaxation of the  $OH(J \ge 9)$  levels in Ar is  $\sim$ 5 times faster than for HF. The Einstein coefficients for OH(v) recently published by Langhoff et al.<sup>24</sup> were found to be superior to those of Mies,<sup>22</sup> as judged by the rate constant measured for  $H + NO_2$  vs the  $H + Cl_2$  reaction as a reference. The dynamics of the H + ClO reaction will be discussed in a future publication.<sup>16</sup> A convenient method was developed to measure the extent of  $H_2$  dissociation by a microwave discharge in a fast flow reactor.

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