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Kinetic Studies of Reactions of Hydrogen Atoms with HCl, Cl₂ and NOCl, and Chlorine Atoms with H₂ and NOCl

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Rate constants for the reaction pair

H+HCl
$$\stackrel{k_t}{\longleftrightarrow}$$
 Cl+H₂

have been measured from 295 to 425 K under pseudo-first-order conditions ($[HCl]_0/[H]_0$ and $[H_2]_0/[Cl]_0 \gg 1$) using the discharge-flow-resonance-fluorescence technique. The rate constants followed the Arrhenius expressions:

$$k_{\rm f} = (2.01 \pm 0.3) \times 10^{-11} \exp \left[-(1790 \pm 140)/T\right]$$

 $k_{\rm r} = (6.00 \pm 0.5) \times 10^{-11} \exp \left[-(2470 \pm 100)/T\right].$

The ratio of these rate constants agrees with the thermodynamic equilibrium constant, suggesting that the complicating wall effects and secondary H-atom reactions observed in previous discharge-flow studies of these reactions have been eliminated.

Similar kinetic studies at room temperature of the reactions:

$$H+Cl_{2} \xrightarrow{k_{2}} HCl+Cl$$

$$H+NOCl \xrightarrow{k_{3}} HCl+NO$$

$$Cl+NOCl \xrightarrow{k_{4}} Cl_{2}+NO$$

gave the rate constants:

$$k_2 = (1.70 \pm 0.26) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

 $k_3 = (1.82 \pm 0.27) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
 $k_4 = (7.2 \pm 2.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The values for k_2 and k_3 are in excellent agreement with those reported by previous discharge-flowresonance-fluorescence studies. The value for k_4 is approximately a factor of two larger than the only other direct determination.

Prior to 1966, the kinetics of the reaction pair

$$H + HCl \underset{k_r}{\overset{k_f}{\longleftrightarrow}} Cl + H_2 \tag{1}$$

were considered to be amongst the best understood for any free atom or radical reactions.¹ It is one of the few gas-phase elementary reactions which has an easily measurable rate constant in both directions. In 1966, Clyne and Stedman² completed the first absolute determination of k_f from 195 to 373 K using a

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discharge-flow system with H-atom detection by HNO chemiluminescence. Their results, coupled with those reported by previous workers,³⁻⁵ indicated that the activation energy for the forward reaction increased with temperature, causing appreciable curvature in an Arrhenius plot. Two years later, Westenberg and de Haas⁶ measured both k_f and k_r independently using a discharge-flow-electron paramagnetic resonance (e.p.r.) system from 195 to 500 K, and although their measurements gave linear Arrhenius plots, they obtained the surprising result that the rate constant ratio, $k_{\rm f}/k_{\rm r}$, was 2–3 times larger than the calculated equilibrium constant. This apparent deviation from the principle of microscopic reversibility gave rise to a number of reports attempting to explain the experimental discrepancy. These have included the speculations that (a) the deviation arose from the inapplicability of microscopic reversibility to this reaction because of a greater probability of obtaining rotationally hot HCl in the reverse reaction than rotationally hot H_2 in the forward reaction;⁶ (b) a non-Boltzman distribution between the $Cl({}^{2}P_{3/2})$ and $Cl(^{2}P_{1/2})$ spin-orbit states during the course of the reverse reaction caused the overall rate of reaction of Cl with H_2 to be less than under equilibrium conditions;^{7,8} (c) because of the concurrent rapid wall reaction, $H + CI \rightarrow HCI$, during the study of the forward reaction, the measured rate constant was actually $2k_{\rm f}$ rather than $k_{\rm f}$,⁹ and (d) the measurements of $k_{\rm r}$ may have been systematically too low because of the regeneration of Cl atoms by the rapid reaction of the product H atoms with undissociated Cl₂ present in the system.¹⁰

Our reanalysis of the data of Westenberg and de Haas⁶ indicates that neither their rate constants nor their error limits were correctly derived from their original data, casting some doubt on the theoretical aspects of their work. Since their method of analysis is still used,¹¹ it is important to demonstrate how errors can be introduced. The determination of a second-order rate constant usually involves measurement of the pseudo-first-order logarithmic decay rate of one reagent (X) in an excess of the other (Y), in either a flowing or static system. The rate constant is defined as d[X]/dt = -k[X][Y], which in pseudo-first-order conditions reduces to $d \ln [X]/dt = -k[Y]$. Sometimes the observed parameter $(d \ln [X]/dt)[Y]^{-1}$ is treated as if it is a statistically independent measurement of k, several of which are then averaged and treated to obtain a standard deviation. However, this procedure gives an incorrect value of k unless the observed reaction behaves exactly as predicted {*i.e.* $d \ln [X]/dt$ (observed) = 0 at [Y] = 0} and in any case gives on averaging an erroneous value of the precision of the estimate of k since each estimate includes the origin as an error-free point. A better experimental value of k and a proper evaluation of the experimental precision can only be obtained by describing the measured rate constant as $\partial(\partial \ln [X]/\partial t)_{[Y]}/\partial [Y]$, or the similar equation obtained by taking the partial differential in the reverse order $\partial(\partial \ln [X]/\partial [Y])_{t}$. The experimental precision is the least-squares value of the slope obtained on the second graph implied by the second differential. This paper gives an example of this analysis procedure. Westenberg and de Haas⁶ give adequate original data for a correct analysis of some of their observations. When applied to $Cl + H_2$ at room temperature, their k_{meas} drops by 11% (more than their declared precision) with an increase in σ from $\pm 5\%$ to $\pm 7\%$. Unfortunately, although their analysis reports precise values of k at other temperatures, the range of $[H_2]$ over which these measurements were made makes it impossible to extract a worthwhile value of $k_{\text{meas.}}$, or even a precision estimate. In essence, their analysis for k depends on a model of how the experiment behaves; unfortunately, their model is incorrect. Also, their precision makes use not only of that model, but also of a presumed error-free point at the origin of the second graph. This usually, but not always,

will give a higher precision than the slope of a line through a set of measured points

 $\partial \ln [X]/\partial t \cdots [Y]$, particularly if the range of [Y] is limited. Recent direct measurements¹²⁻¹⁴ of k_r are in general agreement with the results of Westenberg and de Haas,⁶ suggesting that the reason for the discrepancy lies in the measured value of k_f . Direct determinations^{15,16} of k_f , made with dischargeflow-e.p.r. systems, have resolved the discrepancy with K_{eq} only by postulating the occurrence of enhanced H-atom removal through wall catalysed reactions involving species such as HCl₂ and vibrationally excited HCl, making stoichiometric corrections to the experimentally measured rate constants necessary.

By measuring both k_f and k_r in the same system, using the same method and the same temperature range, any systematic errors in the individual rate constant measurements will be cancelled when taking their ratio. Because of the need¹⁷ for additional study of reaction (1) above 300 K, kinetic measurements of $k_{\rm f}$ and $k_{\rm r}$ were performed at four temperatures between 295 and 425 K.

We also measured the rate constant for the reaction

$$H + Cl_2 \xrightarrow{k_2} HCl + Cl$$
 (2)

using the same system at room temperature and comparing the results with those of the most recent determinations^{18,19} which utilized discharge-flow-resonancefluorescence systems. In addition, the results of the room-temperature kinetic investigations of the reactions

$$H + NOCI \xrightarrow{k_3} NO + HCI$$
(3)

$$Cl + NOCl \xrightarrow{k_4} NO + Cl_2$$
 (4)

are reported. Reactions (3) and (4) are often used²⁰ as titration reactions for determining absolute concentrations of H and Cl atoms. There are only two reported investigations of $k_3^{21,22}$ and they are not in good agreement. The absolute rate for the reaction of Cl with NOCl has been studied in only one previous investigation,²³ for which a value of k_4 was reported approximately a factor of ten larger than an earlier indirect competitive determination.²⁴

EXPERIMENTAL

A detailed description of the flow-tube technique for obtaining quantitative kinetic information for gaseous elementary reactions can be found elsewhere.^{11,20,25} The dischargeflow system used here is illustrated schematically in fig. 1. The 25 mm i.d. flow tube, usually coated with syrupy phosphoric acid to inhibit atom recombination, was operated at pressures between 1 and 6 Torr[†] and at linear flow velocities between ca. 500 and 2000 cm s⁻¹. H or Cl atoms were generated upstream of the reaction zone by a microwave discharge (2450 MHz) in dilute mixtures of H_2 or Cl_2 in helium (99.995%) or argon (99.998%) carrier gas using a discharge bypass arrangement in order to control the low atom flow and to minimize any atomic impurities. For kinetic studies, when very low H-atom concentrations were desired $(<1\times10^{11}$ cm³), the inert carrier gas alone was passed through the discharge. The impurity level of the carrier was large enough to generate significant concentrations of H atoms.

The H or Clatoms were detected at the fixed observation point by resonance fluorescence, using as the excitation source sealed, low pressure (ca. 1 Torr) microwave discharge lamps, similar to those used for in situ stratospheric measurements.^{26,27} The fluorescence cell,

 $\dagger 1 \text{ Torr} = 101 \ 325/760 \text{ Pa}.$



FIG. 1.-Schematic diagram of the discharge-flow kinetic system.

machined from an aluminium block and internally blackened to reduce scattered light, was mounted directly to the flow-tube and pumping system. The Lyman- α radiation (121.6 nm) used to excite H atoms passed through a 6 mm space containing O₂ flowing at atmospheric pressure and a series of collimating baffles before entering the scattering volume. The exciting Cl atom resonance radiation (lines between 133 and 140 nm) passed through a CaF₂ window and a series of collimating light baffles. Resonantly scattered photons were detected at right angles to the lamps with an E.M.I.G. model G-26H315 photomultiplier tube using pulse counting techniques. In order to ensure that the observed fluorescent signal was linearly dependent upon the concentration of atomic species being monitored, absolute Cland H-atom concentrations were estimated using the titration reactions of these species with NOCl. A linear relationship between atom concentration and fluorescence intensity was found for both Cl and H up to $ca. 2 \times 10^{12}$ cm⁻³. Detection limits (S/N = 1) of $ca. 1 \times 10^8$ cm⁻³ for [H] and 5×10^9 cm⁻³ for [Cl] were estimated.

 H_2 (99.999%) was used directly from a cylinder without further purification. Cl_2 (99.5%) was purified by trap-to-trap distillation at 195 K. HCl (99%) was purified by repeated warming, freezing and pumping at 77 K followed by distillation from a trap at 195 K. NO (99.9%) was purified by repeated warming, freezing and pumping at 77 K, discarding the blue-coloured fractions which contained N₂O₃. Adequate purity was assumed when the solid at 77 K was colourless. NOCl was prepared by reaction of an excess of purified NO with a sample of redistilled Cl₂. The NOCl was freed from NO by pumping at 195 K.

RESULTS AND DISCUSSION

The kinetics of all the reactions were studied under pseudo-first-order conditions, e.g. $[HCl]_0/[H]_0$ and $[H_2]_0/[Cl]_0 \gg 1$. The fluorescent signal was always observed to decrease exponentially with increased concentration of added reagent. Typical kinetic plots are shown in fig. 2 and 3 for the reaction of Cl atoms with H₂. Similar plots were obtained for the reactions of Cl with NOCl, and H with HCl, Cl₂ and NOCl. For a given reaction distance (*i.e.* time), $\partial \ln[[Cl]_0/[Cl]])/\partial[H_2]$ was constant (fig. 2) and the value was proportional to reaction distance (fig. 3). Bimolecular rate constants were obtained by multiplying the slopes of plots such as fig. 3 by the measured flow velocity.



FIG. 2.—Plot of ln ([Cl]₀/[Cl]) against [H₂] at various reaction distances relative to the centre of the detection system: •, 15; ×, 25; \bigcirc , 35; •, 45; •, 55 cm. Argon carrier gas; pressure = 1.36 Torr; flow velocity = 961 cm s⁻¹; T = 297 K.



FIG. 3.—Plot of d ln ([Cl]₀/[Cl])/d[H₂] against reaction distance. Argon carrier gas; pressure = 1.36 Torr; flow velocity = 961 cm s⁻¹; T = 297 K.

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$k_{\rm r}/10^{-14}{\rm cm}^3{\rm molecule}^{-1}{\rm s}^{-1}$	pressure/Torr	carrier gas	
1.61	1.12	Ar	
1.54	1.36	Ar	
1.12	1.51	He	
1.53	2.10	Ar	
1.53	2.46	Ar	
1.43	2.47	Ar	
1.49	2.49	Ar	
1.52	2.50	Ar	
1.48	2.50	Ar	
1.57	2.57	Ar	
1.73	2.58	He	
1.37	2.70	Ar	
1.43	3.21	Ar	
1.07	3.21	Ar	
1.30	3.58	He	
1.38	3.61	He	
1.73	4.75	Ar	
1.37	5.45	Ār	

TABLE 1.—RATE-CONSTANT DATA FOR $Cl+H_2 \rightarrow HCl+H$ at 297 K

TABLE 2.—TEMPERATURE DEPENDENCE OF k_r and k_f^a

<i>T</i> /K	$k_{\rm r}/10^{-14}{\rm cm}^3{\rm molecule}^{-1}{\rm s}^{-1}$	$k_{\rm f}/10^{-14}{\rm cm}^3{\rm molecule}^{-1}{\rm s}^{-1}$	
297	1.46 ± 0.22		
324	2.97 ± 0.45		
375	8.33 ± 1.3		
425	17.9 ± 2.7		
294		4.93 ± 0.75	
323		7.15 ± 1.1	
374		17.1 ± 2.6	
424	_	30.3 ± 4.5	

^a The entries in the table are the mean values of the slopes of lines such as those shown in fig. 2. The error limits are an estimated 1σ based on the standard deviation of the observed slopes, and an additional contribution from estimates of systematic errors.

The reaction $Cl+H_2 \rightarrow HCl+H$

The measurement of the absolute reaction rate of Cl with H_2 was undertaken as part of the overall kinetic study of the reaction

$$H + HCl \xrightarrow{k_t} Cl + H_2.$$
(1)

The initial measurements were made at room temperature in both argon and helium carriers and over the pressure range 1-6 Torr. Table 1 lists some individual determinations, yielding k_r $(\pm 1\sigma) = (1.46 \pm 0.22) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ at 297 K when systematic error estimates are also included in the estimated standard deviation. As expected for a bimolecular reaction, no pressure dependence was observed and there was no dependence upon the nature of the inert-gas carrier. Experiments were conducted at temperatures between 297 and 425 K. Table 2

$\frac{A/10^{-11} \text{ cm}^3}{\text{molecule}^{-1}}$	E_{a} /kcal mol ⁻¹	k at 298 K $/10^{-14}$ cm ³ molecule ⁻¹ s ⁻¹	method ^d	ref.
	$k_{\rm r} {\rm Cl} + {\rm H}_2$			
2.0 ± 0.5	4.30 ± 0.20	1.40	d.fe.p.r.	6
5.5 ± 0.5	4.72 ± 0.2	1.90	f.pr.f.	13
2.66 ± 0.42	4.43 ± 0.12	1.50	f.pr.f.	14
3.65 ± 0.17	4.59 ± 0.04	1.59	f.pr.f.	28
6.00 ± 0.5	4.91 ± 0.2	1.50	d.fr.f.	this work
	k_{f} H+HC			
1.55 ^a	3.1 ^a	8.3	d.fc.l.	2
3.8 ± 1.0	3.5 ± 0.2	10.3	d.fe.p.r	6
		~4.3 ^b	d.f.–e.p.r.	15
0.78°	3.18 ± 0.17	3.63	d.fe.p.r.	16
1.81 ± 0.02	3.50 ± 0.03	4.93	f.pr.f.	28
2.01 ± 0.3	3.55 ± 0.28	5.01	d.f.–r.f.	this work
	$A/10^{-11} \text{ cm}^{3}$ molecule ⁻¹ s ⁻¹ 2.0 ± 0.5 5.5 ± 0.5 2.66 ± 0.42 3.65 ± 0.17 6.00 ± 0.5 1.55 ^a 3.8 ± 1.0 0.78 ^c 1.81 ± 0.02 2.01 ± 0.3	$\begin{array}{cccc} A/10^{-11}{\rm cm}^3 & E_a \\ {\rm molecule}^{-1} & k_r{\rm Cl} + {\rm H_2} \\ {\rm 2.0 \pm 0.5} & 4.30 \pm 0.20 \\ {\rm 5.5 \pm 0.5} & 4.72 \pm 0.2 \\ {\rm 2.66 \pm 0.42} & 4.43 \pm 0.12 \\ {\rm 3.65 \pm 0.17} & 4.59 \pm 0.04 \\ {\rm 6.00 \pm 0.5} & 4.91 \pm 0.2 \\ & k_t{\rm H} + {\rm HC} \\ {\rm 1.55}^a & {\rm 3.1}^a \\ {\rm 3.8 \pm 1.0} & {\rm 3.5 \pm 0.2} \\ \hline & 0.78^c & {\rm 3.18 \pm 0.17} \\ {\rm 1.81 \pm 0.02} & {\rm 3.55 \pm 0.28} \end{array}$	$\begin{array}{cccc} A/10^{-11}{\rm cm}^3 & k \ {\rm at} \ 298 \ {\rm K} \\ \hline {\rm molecule}^{-1} & E_a & /10^{-14} \ {\rm cm}^3 \\ \bar {\rm molecule}^{-1} & k_r {\rm Cl} + {\rm H}_2 \\ \hline 2.0 \pm 0.5 & 4.30 \pm 0.20 & 1.40 \\ 5.5 \pm 0.5 & 4.72 \pm 0.2 & 1.90 \\ 2.66 \pm 0.42 & 4.43 \pm 0.12 & 1.50 \\ 3.65 \pm 0.17 & 4.59 \pm 0.04 & 1.59 \\ 6.00 \pm 0.5 & 4.91 \pm 0.2 & 1.50 \\ k_t \ {\rm H} + {\rm HCl} \\ 1.55^a & 3.1^a & 8.3 \\ 3.8 \pm 1.0 & 3.5 \pm 0.2 & 10.3 \\ - & - & -4.3^b \\ 0.78^c & 3.18 \pm 0.17 & 3.63 \\ 1.81 \pm 0.02 & 3.55 \pm 0.28 & 5.01 \\ \hline \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

TABLE 3.—ARRHENIUS PARAMETERS FOR $H + HCl \xrightarrow{k_1}{k_2} Cl + H_2$

^{*a*} Obtained by linear least-squares fit to experimental data, which showed appreciable curvature on an Arrhenius plot. ^{*b*} Obtained by extrapolating to unit stoichiometry.¹⁵ ^{*c*} Obtained using a stoichiometry of two.¹⁶ ^{*d*} d.f. = discharge flow; e.p.r. = electron paramagnetic resonance; f.p. = flash photolysis; r.f. = resonance fluorescence; c.l. = HNO chemiluminescence.

shows the results obtained at four temperatures. They are well represented by the Arrhenius equation

$$k_{\rm r} = (6.00 \pm 0.5) \times 10^{-11} \exp\left[-(2470 \pm 100)/T\right].$$

The Arrhenius parameters for this and other direct investigations of k_r are shown in table 3. The best agreement between our data and those of previous studies is seen on comparison with the data of Watson *et al.*¹³ A comparison with other investigations shows some scatter, especially in the pre-exponential factor. However, in general the agreement between the rate constants calculated from the various Arrhenius expressions is reasonably good, as is indicated by the listed values of k_r at 298 K. Considering the differences in the experimental techniques used to measure k_r , the agreement between the Arrhenius parameters is probably as good as can be expected.

THE REACTION $H+HCl \rightarrow H_2+Cl$

The reaction of H atoms with HCl was studied under nearly identical conditions to the reverse reaction. The measurements of k_f at room temperature were made over the pressure range 1.5-5 Torr in a helium carrier. The experiments were conducted under pseudo-first-order conditions with [H]₀ ranging from 2×10^{10} to 2×10^{11} cm⁻³. No dependence of k_f on either pressure or initial H-atom concentration was observed. Table 4 lists the individual determinations at 294 K giving $k_f = (4.93 \pm 0.75) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹. Experiments were conducted at temperatures between 294 and 424 K. Table 2 lists the results obtained at the four

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$k_{\rm f}/10^{-14}{\rm cm}^3{\rm molecule}^{-1}{\rm s}^{-1}$	pressure/Torr	
5.60	1.56	
4.01	1.58	
4.07	3.45	
5.09	3.57	
5.31	3.72	
4.69	3.72	
5.49	5.11	
5.16	5.11	

TABLE 4.—RATE-CONSTANT DATA FOR $H+HCl \rightarrow Cl+H_2$ at 294 K

temperatures which fit the Arrhenius expression

$$k_{\rm f} = (2.01 \pm 0.3) \times 10^{-11} \exp \left[-(1790 \pm 140)/T\right].$$

The Arrhenius parameters for this and the other direct measurements of k_f are given in table 3. Excellent agreement is seen between our results and those of Miller and Gordon,²⁸ who used a different kinetic technique. The activation energy reported here is essentially the same as that reported by Westenberg and de Haas,⁶ however, the pre-exponential factors differ by approximately a factor of two. The data of Clyne and Stedman² and Ambidge *et al.*¹⁶ disagree with the present results, the former showing appreciable curvature on an Arrhenius plot and the latter being obtained by dividing the experimentally observed rate constants by a derived stoichiometric factor of two. Spencer and Glass¹⁵ also applied a stoichiometric correction to their experimental data.

THE RATIO $k_{\rm f}/k_{\rm r}$

The primary objective of the measurements, in the same system and over the same temperture range, of both the forward and reverse rate constants of reaction (1) was to resolve, if possible, the discrepancy between the experimental rate constant ratios and the calculated equilibrium constants, without the need for applying any stoichiometric corrections to the experimental data. Table 5 compares rate constant ratios, calculated from the experimental Arrhenius expressions obtained in direct investigations of both k_t and k_r , with the thermodynamic K_{eq} at four temperatures between 200 and 500 K. As indicated, the results of both this work and the investigation by Miller and Gordon²⁸ give ratios in good agreement with the equilibrium values. The data of Westenberg and de Haas⁶ are larger by a factor of ca. 2–3 over the entire temperature range. Spencer and Glass¹⁵ and Ambidge et al.¹⁶ suggest that the measurements of k_t by Westenberg and de Haas⁶ were enhanced by secondary reactions of H atoms at the reactor walls and that the experimental rate constant ratios should be lowered by a factor of ca. 2, giving values in better agreement with the present results.

By working at H-atom concentrations approximately two orders of magnitude smaller than in the previous e.p.r. investigations, these secondary reactions have apparently been avoided. This is confirmed by our agreement with the results of an investigation²⁸ of reaction (1) performed using a flash-photolysis-resonance-fluorescence kinetic system where wall reactions are unimportant. We conclude from the present study that there is no apparent violation of the principle of

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		kt/kr		
<i>T</i> /K	ref. (6)	ref. (28)	this work	$(calc.)^{b}$
200	14.4	7.6	9.9	8.28
300	7.4	3.1	3.2	3.27
400	5.3	2.0	1.8	2.06
500	4.3	1.5	1.3	1.56

TABLE 5.—COMPARISON BETWEEN CALCULATED AND EXPERIMENTAL RATE-CONSTANT RATIOS⁴

^a Rate-constant ratios are calculated for the four temperatures shown based on the Arrhenius parameters given in the studies cited. ^b Thermodynamic data from JANAF Thermochemical Tables, ed. D. R. Stull and H. Prophet, NSRDS-NBS 37, 1971. Essentially identical values can be obtained from modern spectroscopic data.

microscopic reversibility for the reaction system $H + HCl \rightleftharpoons Cl + H_2$. This is important since such equilibrium considerations are often used under conditions when they are not subject to experimental tests.

REACTIONS OF H WITH Cl_2 and NOCl

The reaction

$$H+Cl_2 \xrightarrow{k_2} HCl+Cl$$
(2)

was studied at room temperature. The results of 10 experiments performed at ca. 1 Torr gave the rate constant $k_2 = (1.70 \pm 0.26) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ at 295 K. This result is in good agreement with the room-temperature results, calculated from their Arrhenius expressions, of Wagner *et al.*, ¹⁸ $k_2 = (1.88 \pm 0.25) \times 10^{-11}$, and of Bemand and Clyne, ¹⁹ $k_2 = (2.01 \pm 0.32) \times 10^{-11}$, obtained in discharge-flow-resonance-fluorescence systems similar to ours. However, these previous results and the present work are in poor agreement with the results of Ambidge *et al.*, ²⁹ $k_2 = (7.0 \pm 0.14) \times 10^{-12}$, obtained in a discharge-flow-e.p.r. system. Possible reasons for this discrepancy have been discussed before^{18,19} and will not be presented here. The good agreement between the result obtained here for k_2 and those obtained in the earlier discharge-flow-resonance-fluorescence studies is a good indication of the accuracy of the rate-constant determinations made in the present system.

The bimolecular reaction of H with nitrosyl chloride is important in laboratory kinetic studies as a titration reaction to determine absolute concentrations of H atoms. Despite its usefulness as a titration reaction, there have been only two reported absolute investigations^{21,22} of the rate constant for the reaction

 $H + NOC1 \xrightarrow{k_3} HC1 + NO$ (3)

which are not in good agreement. In an attempt to clarify this situation, reaction (3) was studied at room temperature under pseudo-first-order conditions.

The rate constant was measured in the flow tube coated with phosphoric acid, conditions under which the unit stoichiometry of the reaction has been confirmed.^{2,21} The result of 25 experiments at *ca.* 2 Torr gave the rate constant

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 $k_2 = (1.82 \pm 0.27) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 294 \text{ K}$. This result is in good agreement with the value obtained by Wagner *et al.*,²² $k_3 = (1.61 \pm 0.25) \times 10^{-11}$, in a discharge-flow-resonance-fluorescence system, but significantly lower than that obtained mass spectroscopically,²¹ $k_3 = (2.7 \pm 0.5) \times 10^{-11}$. It is difficult to identify a definite reason for the discrepancy. Dunn *et al.*²¹ reported difficulties in the measurement of k_3 due to the low sensitivity of the mass spectrometer for NOCl, which required the study to be run at higher reagent concentrations than used here. We therefore consider their results to be less reliable than those obtained with the more sensitive technique. The excellent agreement between the room-temperature rate constants of this work and of Wagner *et al.*²² gives confidence in the Arrhenius expression, $k_3 = 7.6 \times 10^{-11} \exp \left[-(457 \pm 72)/T\right]$, reported by these workers.

REACTION OF Cl WITH NOCL

The absolute rate for the reaction

$$Cl + NOCl \xrightarrow{\kappa_4} NO + Cl_2$$
 (4)

has been studied in only one previous investigation,²³ which reported a value of k_4 , a factor of *ca*. 10 larger than an earlier indirect competitive determination.²⁴ The scarcity of available rate-constant data for this important titration reaction led us to measure k_4 under pseudo-first-order conditions at room temperature.

The results of 20 experiments at *ca*. 1 Torr gave the rate constant $k_4 = (7.2 \pm 2.4) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. This value is much larger than reported by Burns and Dainton,²⁴ $k_4 = 3.2 \times 10^{-12}$. It is also larger than that reported by Clyne and Cruse,²³ $k_4 = (3.0 \pm 0.5) \times 10^{-11}$. As discussed by these workers, the competitive study of Burns and Dainton was likely to have serious systematic errors causing the rate constant k_4 to be underestimated. The difference between the result of this work and that of Clyne and Cruse²³ is surprising since the two studies were done under very similar conditions. Because of the rapidity of reaction (4), it is possible that pseudo-first-order conditions were barely achieved in this work. However, this would lead to an underestimate of the rate constant. The unit stoichiometry for reaction (4) has been confirmed up to $[Cl] = 2.4 \times 10^{13} \text{ cm}^{-3}$,³⁰ and there are apparently no important secondary reactions which could cause an enhancement of the measured rate constant. What is needed is an independent absolute measurement of this reaction using a different experimental technique, *i.e.* flash photolysis, to help resolve and improve upon the previous determinations.

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