NASA TECHNICAL NOTE

NASA TN D-6495

RATE MEASUREMENTS FOR THE REACTION
OF HYDROGEN CHLORIDE AND DEUTERIUM
CHLORIDE WITH ATOMIC OXYGEN

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • SEPTEMBER 1971

1. Report No. NASA TN D-6495	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle RATE MEASUREMENTS FOR THE REACTION OF HYDROGEN CHLORIDE AND DEUTERIUM CHLORIDE WITH ATOMIC OXYGEN		5. Report Date September 1971
		6. Performing Organization Code
7. Author(s) Edgar L. Wong and Frank E. Belles		8. Performing Organization Report No. E-6234
		10. Work Unit No. 129-01
9. Performing Organization Name and Address Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135		11. Contract or Grant No.
		13. Type of Report and Period Covered Technical Note
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

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17. Key Words (Suggested by Author(s)) Reaction kinetics Mass spectrometer	18. Distribution Statement Unclassified - unlimited

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 22	22. Price* $3.00

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SUMMARY

A mass-spectrometric stirred-reactor technique was used to measure the rate of the $O + HCl \xrightarrow{k_1} OH + Cl$ reaction for the temperature range of 356 to 628 K. Reaction products observed were Cl-atom, O_2, H_2, some H_2O, and a trace of Cl_2. The rate constant was found to be $(1.13 \pm 0.16) \times 10^{13} e^{(-7100 \pm 130)/RT}$ cm^3 $mole^{-1}$ sec^{-1}. The measured activation energy was about eight times larger than the value predicted by Mayer and Schieler.

The corresponding reaction $O + DCl \xrightarrow{k_i} OD + Cl$ was also investigated and its rate constant was found to be $(3.74 \pm 0.60) \times 10^{12} e^{(-6800 \pm 170)/RT}$ cm^3 $mole^{-1}$ sec^{-1}.

On the basis of the H_2O produced in the $O + HCl$ reaction an activation energy of about 21 000 joules per mole (5000 cal/mole) was obtained for the $OH + HCl \longrightarrow H_2O + Cl$ reaction. This value can be compared with the estimated value of 27 000 joules per mole (6500 cal/mole) in the literature.

INTRODUCTION

Reactions between hydrogen halides and combustion chain carriers, such as oxygen atoms, occur in many processes. Some of these are flame extinction by halogenated agents, the combustion of plastics, and the chemistry of scavenging agents in the combustion of leaded fuels.

Although these reactions occur widely and may have significant kinetic effects, it is difficult to assess their importance because their rates have not been measured. For instance, in a recent paper on the chemistry of flame extinction by halogenated agents (ref. 1) the possible importance of reactions of hydrogen halides with atomic oxygen could only be evaluated by resorting to theoretical rate calculations (ref. 2). At the

present time such calculations are too unreliable to replace direct measurements. To a large extent, the uncertainty of these computed rate constants is due to the fact that there are not enough examples of reactions whose rates have been both computed and measured.

This report describes measurements of rate constants for the reaction of atomic oxygen with hydrogen chloride (O + HCl) for the temperature range of 356 to 628 K, using a mass-spectrometric stirred-reactor technique (ref. 3). These appear to be the first such measurements; the only previous study of this reaction (ref. 4) was at room temperature and no reliable rates were obtained. The present results are compared with the theoretical computed rate and activation energy reported in reference 2. To provide more data to compare with theory, the rate of the corresponding reaction with deuterium chloride (O + DCl) was measured over a similar temperature range.

EXPERIMENTAL PROCEDURE

Apparatus

The apparatus consisted of a 300-cubic-centimeter Pyrex reactor connected to a time-of-flight mass spectrometer, as shown in figure 1. This reactor and its inlet tubes were wrapped with electrical heating tape so that they could be heated to any desired temperature up to about 650 K. Further description of this technique is given in reference 3.

Gases

Oxygen and argon had a stated minimum purity of 99.9 percent and were used without further purification. HCl, DCl, and nitrogen dioxide (NO_2) had stated purities of 99.3, 99.0, and 95 percent, respectively, and were further purified by fractionation before using.

Oxygen atoms were produced by flowing a gas mixture of 1.83-percent O_2 in argon at a pressure of 0.8 torr through a microwave discharge (fig. 1). The flow rate of this mixture was kept at 1.38 cubic centimeters per second at standard conditions of 0° C and 760 torr. Through inlet tube 2, increasing amounts of HCl or DCl were metered into the reactor. For each addition of HCl or DCl, the amounts of reactant gases consumed and reaction products produced were measured mass spectrometrically.
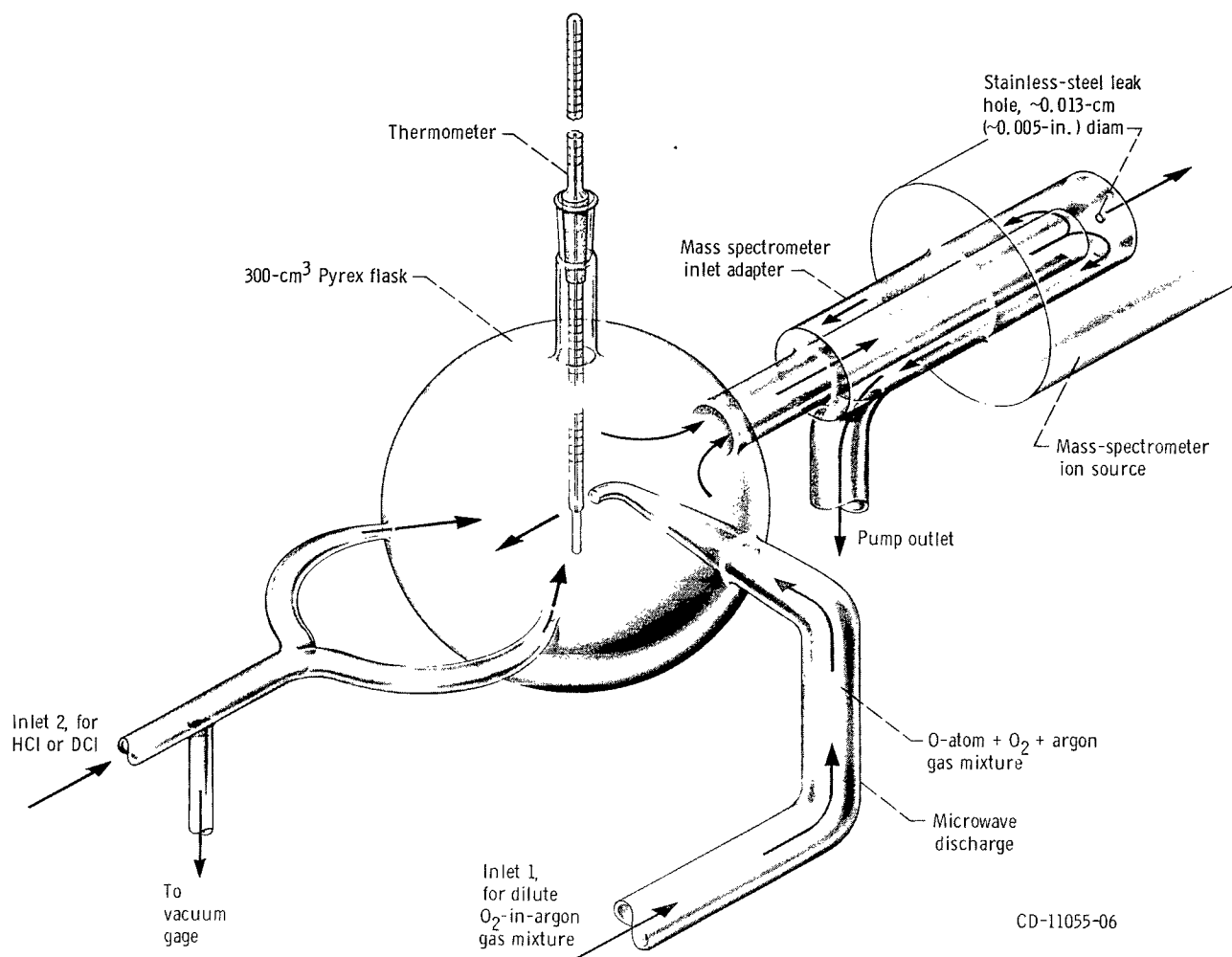
Figure 1. - Stirred reactor and connection to mass spectrometer.

Calibration

Mass-spectrometer sensitivities for O-atom, O_2, H_2, HCl, and DCl were needed for this study. O-atom sensitivity was obtained by the $O + NO_2 \longrightarrow NO + O_2$ titration technique (ref. 5). Sensitivities for O_2, H_2, HCl, and DCl were obtained by the usual mass-spectrometer calibration technique of adding known amounts of these gases into the gas flow and noting the effects on their respective peaks.

(a) Temperature, 325 K.
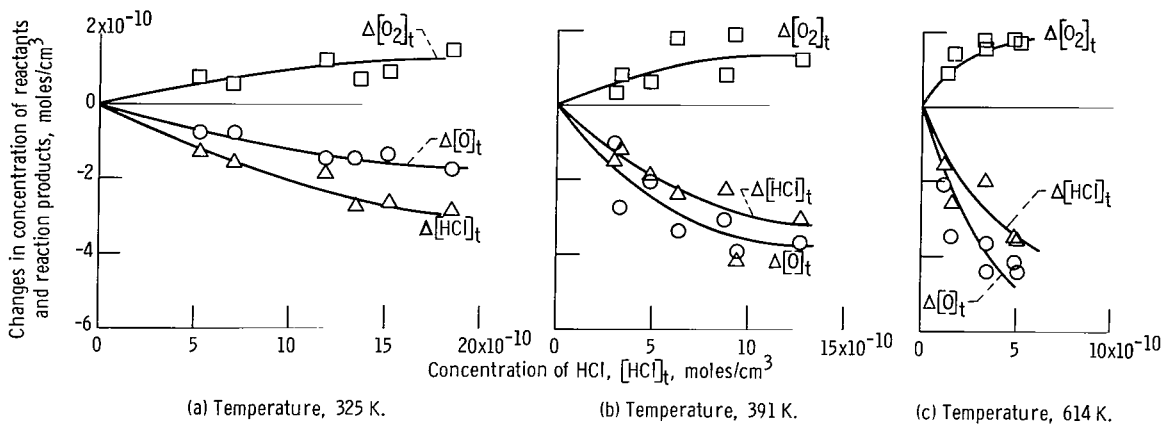
(b) Temperature, 391 K.

(c) Temperature, 614 K.

Figure 2. – Stoichiometric analyses of O + HCl reaction.

(a) Temperature, 348 K.

(b) Temperature, 497 K.
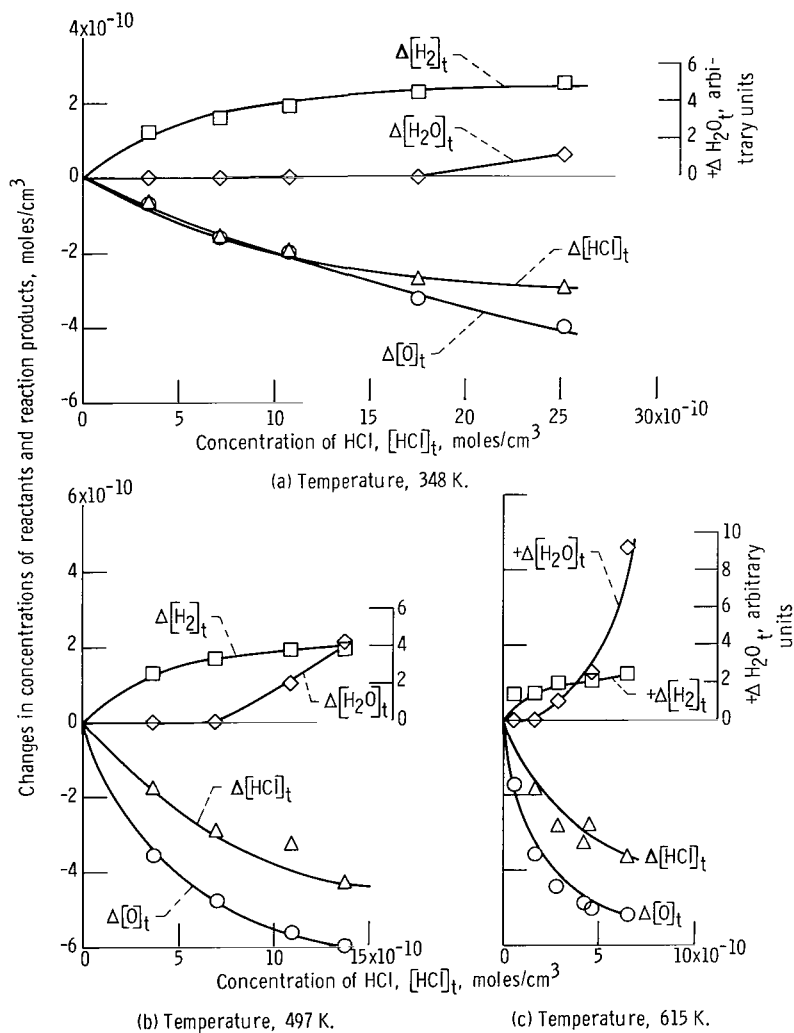
(c) Temperature, 615 K.

Figure 3. – Stoichiometric analyses of O + HCl reaction.

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Mass-Spectrometric Reaction Product Analyses

In order to calculate a rate constant k_1 for the O + HCl reaction, mass-spectrometric reaction product analyses were first conducted. These analyses showed that significant amounts of both O-atom and HCl were consumed to produce the following reaction products: Cl-atom, O_2, H_2, some H_2O, and a trace of chlorine (Cl_2). The results of these analyses are shown in figures 2 and 3, in which the change in concentration of reactants ($\Delta[\text{reactants}]_t$) or reaction products ($\Delta[\text{reaction product}]_t$) in moles per cubic centimeter at reaction time t is plotted against the concentration of HCl ($HCl)_t$ in moles per cubic centimeter at reaction time t. In general the essential findings are as follows:

(1) The amount of HCl consumed ($-\Delta[HCl]_t$) is equal to, or larger than, the amount of O-atom consumed ($-\Delta[O]_t$) at the lowest temperature and is smaller than $-\Delta[O]_t$ at the higher temperatures (figs. 2 and 3).

(2) The amount of O_2 produced ($\Delta[O_2]_t$) is about equal to $-\frac{1}{2}\Delta[O]_t$ at the lowest temperature and is slightly smaller than $-\frac{1}{2}\Delta[O]_t$ at the higher temperatures (fig. 2).
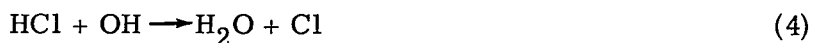
(3) The amount of H_2 produced ($\Delta[H_2]_t$) is about the same for the two lower temperatures and decreases at the higher temperatures. The $\Delta[H_2]_t$ levels off at about the same $[HCl]_t$ at which H_2O appears as a reaction product (fig. 3).

(4) The amount of H_2O produced ($\Delta[H_2O]_t$) is dependent on both $[HCl]_t$ and temperature. At the lower temperatures $\Delta[H_2O]_t$ is small and occurs only at very high values of $[HCl]_t$. As the temperature is increased, $\Delta[H_2O]_t$ increases and occurs at smaller values of $[HCl]_t$. On the basis of the relative $\Delta[H_2O]_t$ measurements in activation energy of about 21 000 joules per mole (5000 cal/mole) can be deduced for the OH + HCl $\longrightarrow$ H_2O + Cl reaction. This value can be compared with the estimated value of 27 000 joules per mole (6500 cal/mole) reported in reference 6 (fig. 3).

Reaction Mechanism for O + HCl Reaction

On the basis of the preceding findings the following reaction mechanism is proposed:

$$\text{HCl} + \text{O} \longrightarrow \text{OH} + \text{Cl} \tag{1}$$

$$\text{OH} + \text{O} \longrightarrow O_2 + \text{H} \tag{2}$$

$$\text{HCl} + \text{H} \longrightarrow H_2 + \text{Cl} \tag{3}$$

$$HCl + OH \longrightarrow H_2O + Cl \tag{4}$$

$$O + O + M \longrightarrow O_2 + M \tag{5}$$

$$O + O_2 + M \longrightarrow O_3 + M \tag{6}$$

$$O_3 + O \longrightarrow 2O_2 \tag{7}$$

$$Cl + Cl + M \longrightarrow Cl_2 + M \tag{8}$$

$$Cl_2 + O \longrightarrow OCl + Cl \tag{9}$$

$$OCl + O \longrightarrow O_2 + Cl \tag{10}$$

$$H + Cl_2 \longrightarrow HCl + Cl \tag{11}$$

In this reaction scheme, reaction (1) is the initiating reaction. Reaction (1) and the fast reaction (3) (ref. 7) are mainly responsible for Cl-atom production. Reaction (4) (ref. 6) is included for the production of H_2O; but since it has to compete with reaction (2), which is very fast (ref. 8), reaction (4) becomes important for Cl and H_2O production only for the condition in which the ratio of $[HCl]_t/[O]_t$ is relatively large, or at the higher temperatures when k_4 becomes competitive with k_2.

Reaction (2) is very fast (ref. 8) and is mainly responsible for the O_2 production; reactions (5), (7), and (10) are minor contributors. For our experimental condition, using values of k_2 from reference 8, k_5 and k_7 from reference 9, k_8 from reference 10, and k_{10} from reference 11, and assuming steady-state approximation for ozone (O_3) and the chlorine oxide radical (OCl), calculation indicated that reaction (2) is responsible for about 90 percent of the O_2 production at the lowest temperature and about 95 percent at the higher temperatures.

Reaction (3), being very fast (ref. 7), is responsible for the H_2 production. Reaction (8) is responsible for the trace of Cl_2 as a reaction product. If we assume that $[Cl]_t$ is approximately equal to the total O-atom consumption ($-\Delta[O]_t$), calculation making use of reaction (8) (ref. 10) indicated that $[Cl_2]_t$ was about 10^{-13} moles per cubic centimeter. This value is about 1/1000th of that for O-atom or HCl in our system. Even through $[Cl_2]_t$ was very small, reactions (9) and (10) are included because both of these reactions are very fast (ref. 10).

Reaction (11) is another very fast reaction (ref. 6) and is included to explain why $-\Delta[HCl]_t < -\Delta[O]_t$ at the higher temperatures. At the higher temperatures this reaction regenerates HCl to compensate for its loss through reaction (4).

Calculation of Rate Constants

On the basis of the preceding reaction scheme, an approximate rate constant k_{1a} can be deduced for the $O + HCl \rightarrow OH + Cl$ reaction. This k_{1a} is based on the assumptions that reaction (4) is of minor importance and that all the O-atoms are consumed by reactions (1) and (2). Both of these assumptions are supported by our findings that reaction (4) is important mostly at higher ratio values of $[HCl]_t/[O]_t$, and that reactions other than (1) and (2) consume a minor amount of the O-atoms. Thus, the total O-atom consumption rate, $-d[O]/dt$, is equal to the expression

$$- \frac{d[O]}{dt} = k_{1a}[O]_t[HCl]_t + k_2[O]_t[OH]_t \tag{12}$$

Then, by assuming the steady-state approximation for OH, equation (12) becomes

$$- \frac{d[O]}{dt} = 2k_{1a}[O]_t[HCl]_t \tag{13}$$

For a stirred reactor, the differentials in equation (13) are replaced by finite difference terms (ref. 12), and equation (13) can be rewritten as

$$- \frac{\Delta[O]_t}{\Delta t} = 2k_{1a}[O]_t[HCl]_t \tag{14}$$

The approximate rate constant k_{1a} in cm^3 $mole^{-1}$ sec^{-1} can be obtained from this equation

$$k_{1a} = \frac{1}{2}\left(- \frac{\Delta[O]_t}{[O]_t}\right)\frac{1}{\Delta t[HCl]_t} \tag{15}$$

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In equation (15), $-\Delta[O]_t/[O]_t$ is the fraction of total O-atom consumed and $-\Delta[O]_t$ is equal to $[O]_0 - [O]_t$, where $[O]_0$ is the O-atom concentration before any reaction due to added HCl, and Δt is the residence time. Since $-\Delta[O]_t/[O]_t$ and $[HCl]_t$ were measured mass spectrometrically and Δt can be computed, k_{1a} can be calculated.

Having obtained k_{1a}, a rate constant k_1 for the O + HCl reaction can be deduced based on a more detailed analysis of the same reaction scheme. For this analysis, $-d[O]/dt$ is equal to the following expression:

$$\frac{-d[O]}{dt} = k_1[O]_t[HCl]_t + k_2[O]_t[OH]_t + 2k_5[O]_t^2[M] + k_6[O]_t[O_2]_t[M] + k_7[O_3]_t[O]_t$$

$$+ k_9[Cl_2]_t[O]_t + k_{10}[OCl]_t[O]_t \qquad (16)$$

and the rate of O_2 production $(d[O_2]/dt)$ is

$$\frac{d[O_2]}{dt} = k_2[O]_t[OH]_t + k_5[O]_t^2[M] - k_6[O_2]_t[O]_t[M] + 2k_7[O_3]_t[O]_t + k_{10}[OCl]_t[O]_t$$

$$\qquad (17)$$

Then by assuming the steady-state approximation for O_3 and OCl, equation (16) becomes

$$\frac{-d[O]}{dt} = k_1[O]_t[HCl]_t + k_2[O]_t[OH]_t + 2k_5[O]_t^2[M] + 2k_6[O_2]_t[O]_t[M] + 2k_9[Cl_2]_t[O]_t$$

$$\qquad (18)$$

and equation (17) becomes

$$\frac{d[O_2]}{dt} = k_2[O]_t[OH]_t + k_5[O]_t^2[M] + k_6[O_2]_t[O]_t[M] + k_9[O]_t[Cl_2]_t \qquad (19)$$

Equation (18) can now be modified by the proper substitution of equation (19) and can be rewritten as

$$\frac{-d[O]}{dt} = k_1[O]_t[HCl]_t + \frac{d[O_2]}{dt} + k_5[O]_t^2[M] + k_6[O_2]_t[O]_t[M] + k_9[O]_t[Cl_2]_t \qquad (20)$$

For a stirred reactor (ref. 12), equation (20) can be rewritten as

$$\frac{-\Delta[O]_t}{\Delta t} = k_1[O]_t[HCl]_t + \frac{\Delta[O_2]_t}{\Delta t} + k_5[O]_t^2[M] + k_6[O_2]_t[O]_t[M] + k_9[O]_t[Cl_2]_t \quad (21)$$

In equation (21), $\Delta[O_2]_t$ is the O_2 produced due to added HCl. Equation (21) can now be rearranged to obtain the following expression for k_1 in cm^3 $mole^{-1}$ sec^{-1}:

$$k_1 = \left\{ \frac{(-\Delta[O]_t)}{[O]_t} - \frac{\Delta[O_2]_t}{[O]_t} - k_5 \Delta t[O]_t[M] - k_6 \Delta t[O_2]_t[M] - k_9 \Delta t[Cl_2]_t \right\} \frac{1}{\Delta t[HCl]_t}$$

$$(22)$$

In equation (22) the term $(-\Delta[O]_t)$ is again equal to $[O]_0 - [O]_t$. The rate constant k_1 can be calculated since $-\Delta[O]_t/[O]_t$, $\Delta[O_2]_t$, and $[HCl]_t$ were measured and both Δt and $[Cl_2]_t$ can be evaluated. Values of k_5 and k_6 were from reference 9 and k_9 was from reference 11.

The corresponding reaction of $O + DCl \xrightarrow{k_i} OD + Cl$ was analyzed in a similar manner and its rate constant (k_i or k_{ia}) was also derived from an expression like equation (15) or (22) but with the term $[HCl]_t$ replaced by $[DCl]_t$.

RESULTS AND DISCUSSION

Consumption of O-atoms Due to Added HCl and Added DCl

The fraction of total O-atom consumed $(-\Delta[O]_t/[O]_t)$ due to added HCl is tabulated in table I and shown in figure 4 as a plot of $-\Delta[O]_t/[O]_t$ against $[HCl]_t$. For the temperatures investigated, straight lines beginning at the origin can be drawn through the data. Scatter of these measurements can be obtained by noting that most of the data deviated by less than 10 percent from the drawn lines.

The total O-atom consumed due to added DCl is tabulated in table II and shown in figure 5 as a plot of $-\Delta[O]_t/[O]_t$ against $[DCl]_t$. Again straight lines beginning at the origin were drawn through the data to separate the results obtained at the different temperatures. In general, the scatter of this data was about 10 percent or less with the exception of the 366 to 376 K data, which showed a scatter of 10 to 20 percent.

A comparison of figures 4 and 5 shows that for about the same given temperature the O-atom consumed due to added HCl is about twice that due to added DCl.

TABLE I. - RATE MEASUREMENT DATA FOR O + HCl REACTION

Run	Concentration of HCl at reaction time t, $[HCl]_t$, moles/cm^3	Initial O-atom concentration prior to reaction, $[O]_o$, moles cm^3	Temperature, T, K	Fraction of total O-atom consumed, $\frac{-\Delta[O]_t}{[O]_t}$	O_2 production due to added HCl, $\frac{\Delta[O_2]_t}{[O]_t}$	Residence time, Δt, sec	Correction to total O-atom consumption $k_5 \Delta t[O]_t[M]$ A	$k_6 \Delta t[O_2]_t[M]$ B	$k_9 \Delta t[Cl_2]_t$ C	A + B + C	Rate constant, k_1', cm^3 mole^{-1} sec^{-1}	Rate constant, k_{1a}', cm^3 mole^{-1} sec^{-1}
1a	3.52×10^{-10}	9.21×10^{-10}	353	0.072	0.040	0.172	12.5×10^{-4}	5.43×10^{-4}	7.42×10^{-4}	2.54×10^{-3}	4.86×10^8	5.93×10^8
1b	5.75	9.15	353	.124	.061	.171	11.8	5.73	19.4	3.69	6.03	6.30
1c	8.90	9.19	353	.179	.074	.171	11.4	6.02	37.8	5.53	6.54	5.88
1d	12.6	9.04	355	.238	.112	.169	10.0	6.24	57.1	7.34	5.56	5.57
1e	17.6	9.00	356	.308	.170	.168	10.1	7.04	84.1	10.1	4.32	5.20
2a	4.69	9.04	358	.088	.049	.169	11.2	5.07	9.95	2.62	4.59	5.55
2b	8.72	9.05	358	.156	.108	.169	10.7	6.08	28.1	4.49	2.95	5.29
2c	13.9	8.92	358	.266	.140	.166	9.45	6.21	63.7	7.93	5.14	5.79

Average k_1 = $(5.00 \pm 0.80)\times10^8$ ±16 percent
Average k_{1a} = $(5.69 \pm 0.28)\times10^8$ ±5 percent

Run												
3a	5.38×10^{-10}	7.62×10^{-10}	424	0.359	0.142	0.142	4.68×10^{-4}	2.23×10^{-4}	60.4×10^{-4}	6.73×10^{-3}	2.75×10^9	2.35×10^9
3b	9.08	7.60	425	.590	.179	.141	3.98	2.27	119	12.5	3.11	2.30
3c	13.5	7.47	426	.842	.323	.139	3.33	2.67	168	17.4	2.68	2.25
4a	2.54	7.62	428	.163	.049	.142	5.40	1.71	17.0	2.41	3.09	2.26
4b	5.38	7.55	428	.351	.153	.140	4.54	2.19	55.5	6.23	2.55	2.34
4c	9.01	7.51	429	.587	.287	.140	3.85	2.44	114	12.0	2.28	2.33
4d	11.9	7.44	429	.783	.332	.138	3.35	2.68	153	15.9	2.65	2.39

Average k_1 = $(2.73 \pm 0.20)\times10^9$ ±7 percent
Average k_{1a} = $(2.32 \pm 0.04)\times10^9$ ±2 percent

Run												
5a	1.44×10^{-10}	7.11×10^{-10}	498	0.206	0.063	0.122	3.28	0.68×10^{-4}	18.0×10^{-4}	2.19×10^{-3}	8.00×10^9	5.84×10^9
5b	2.34	7.09	498	.378	.143	.122	2.87	.85	45.5	4.92	8.04	6.61
5c	4.33	7.02	499	.706	.253	.120	2.24	.99	98.6	10.2	8.53	6.80
5d	7.55	7.02	499	1.24	.404	.120	1.73	1.11	115	11.8	9.10	6.85
5e	10.2	7.02	500	1.63	.507	.120	1.49	1.17	226	22.8	8.95	6.63
6a	2.29	7.05	501	.397	.149	.121	2.77	.84	47.2	5.08	8.74	7.16
6b	4.32	6.99	501	.577	.272	.120	2.41	1.06	76.0	7.95	5.73	5.58
6c	6.33	7.01	502	.988	.451	.120	1.93	1.27	142	14.6	6.87	6.50
6d	9.94	6.91	502	1.67	.660	.119	1.41	1.31	215	21.7	8.36	7.07

Average k_1 = $(8.04 \pm 0.80)\times10^9$ ±10 percent
Average k_{1a} = $(6.56 \pm 0.39)\times10^9$ ±6 percent

Run												
7a	0.84×10^{-10}	5.80×10^{-10}	629	0.524	0.174	0.097	1.19	0.294×10^{-4}	31.5×10^{-4}	3.30×10^{-3}	4.27×10^{10}	3.49×10^{10}
7b	1.97	5.77	629	1.23	.469	.096	.803	.405	78.0	7.92	3.98	3.25
7c	3.94	5.72	629	2.68	.953	.095	.479	.452	131	13.2	4.58	3.58
7d	6.11	5.72	630	3.85	1.35	.095	.366	.476	157	15.8	4.28	3.32
8a	1.85	5.76	630	1.17	.495	.096	.821	.421	73.7	7.50	3.75	3.28
8b	2.80	5.73	631	1.72	.703	.095	.644	.445	100	10.1	3.79	3.24
8c	4.09	5.76	631	2.45	.965	.096	.520	.483	132	13.3	3.75	3.12
8d	6.73	5.69	631	3.85	1.49	.095	.361	.512	158	15.9	3.67	3.02
9a	1.36	5.78	630	.87	.335	.096	.957	.364	53.1	5.44	4.05	3.32
9b	2.99	5.73		1.84	.619	.096	.623	.397	106	10.7	4.22	3.21
9c	4.69	5.68		2.91	1.09	.095	.443	.465	134	13.5	4.05	3.27
9d	6.72	5.70		4.10	1.54	.095	.347	.500	160	16.1	3.99	3.22

Average k_1 = $(3.96 \pm 0.21)\times10^{10}$ ±5 percent
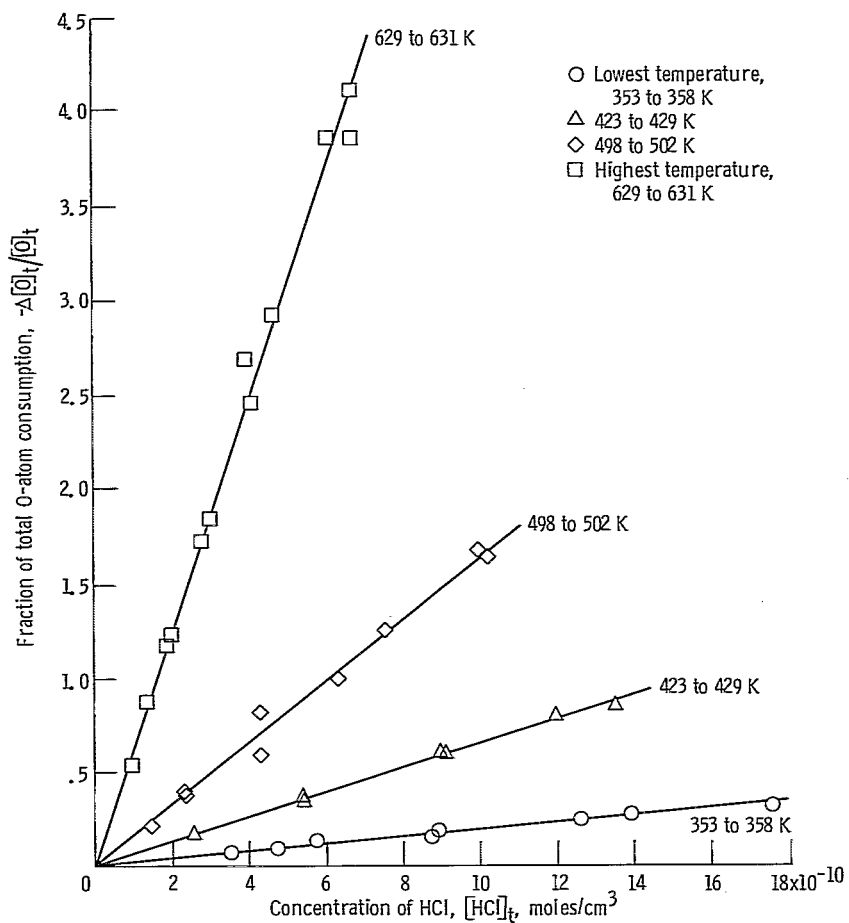Average k_{1a} = $(3.25 \pm 0.10)\times10^{10}$ ±3 percent

Figure 4. – O-atom consumption for O + HCl reaction.

TABLE II. - RATE MEASUREMENT DATA FOR O + DCl REACTION

Run	Concentration of DCl at reaction time t, $[DCl]_t$, moles/cm³	Initial O-atom concentration prior to reaction, $[O]_0$, moles/cm³	Temperature, K	Fraction of total O-atom consumption, $\frac{\Delta[O]_t}{[O]_t}$	O_2 produced due to added DCl, $\frac{\Delta[O_2]_t}{[O]_t}$	Residence, Δt, sec	Correction to total O-atom consumption			A + B + C	Rate constant, k_i, cm³ mole⁻¹ sec⁻¹	Rate constant, k_{ia}, cm³ mole⁻¹ sec⁻¹
							$k_5 \Delta t[O]_t[M]$ A	$k_6 \Delta t[O_2]_t[M]$ B	$k_9 \Delta t[Cl_2]_t$ C			
1a	9.65×10^{-10}	10.4×10^{-10}	366	0.144	0.033	0.164	11.3×10^{-4}	2.51×10^{-4}	3.31×10^{-4}	1.72×10^{-3}	6.92×10^8	4.56×10^8
1b	21.2	10.1	368	.225	.071	.160	10.2	2.87	6.19	1.92	4.47	3.30
1c	41.2	9.86	369	.299	.095	.156	9.39	3.01	9.14	2.15	3.15	2.33
1d	39.3	9.85	371	.336	.083	.156	9.10	2.83	10.5	4.10	4.10	2.75
											Average k_i = $(4.66 \pm 1.13) \times 10^8$ ±24 percent	Average k_{ia} = $(3.24 \pm 0.70) \times 10^8$ ±22 percent
2a	4.23×10^{-10}	10.2×10^{-10}	374	0.043	0.018	0.161	11.4×10^{-4}	1.99×10^{-4}	$0.918 \cdot 10^{-4}$	1.43×10^{-3}	3.46×10^8	3.16×10^8
2b	10.0	10.1	374	.129	.027	.161	10.7	2.13	2.27	1.51	6.20	3.98
2c	19.0	9.95	375	.212	.056	.158	9.67	2.40	5.31	1.74	5.14	3.53
2d	27.5	9.69	375	.250	.078	.154	8.90	2.54	6.27	1.77	4.01	2.95
2e	40.6	9.66	376	.323	.124	.153	8.61	3.01	9.49	2.11	3.17	2.60
											Average k_i = $(4.40 \pm 0.92) \cdot 10^8$ ±21 percent	Average k_{ia} = $(3.24 \pm 0.48) \cdot 10^8$ ±15 percent
3a	11.9×10^{-10}	8.17×10^{-10}	432	0.326	0.102	0.137	4.87×10^{-4}	1.44×10^{-4}	5.79×10^{-4}	1.21×10^{-3}	1.37×10^9	1.00×10^9
3b	18.6	8.02	435	.484	.174	.132	4.15	1.62	9.24	1.50	1.26	.99
3c	27.1	7.87	436	.675	.240	.132	3.62	1.75	13.8	1.91	1.21	.94
											Average k_i = $(1.28 \pm 0.07) \cdot 10^9$ ±6 percent	Average k_{ia} = $(0.98 \pm 0.02) \cdot 10^9$ ±2 percent
4a	5.73×10^{-10}	8.15×10^{-10}	442	0.190	0.052	0.137	$5.23 \cdot 10^{-4}$	$1.51 \cdot 10^{-4}$	2.46×10^{-4}	0.920×10^{-3}	$1.75 \cdot 10^9$	1.21×10^9
4b	12.1	8.05	443	.312	.141	.135	4.64	1.49	5.24	1.14	1.04	.96
4c	21.0	7.87	445	.529	.207	.132	3.85	1.57	10.3	1.57	1.16	.96
4d	26.1	7.79	447	.751	.175	.132	3.35	1.37	15.6	2.03	1.66	1.09
											Average k_i = $(1.40 \pm 0.33) \cdot 10^9$ ±24 percent	Average k_{ia} = $(1.06 \pm 0.08) \cdot 10^9$ ±8 percent
5a	3.24×10^{-10}	7.70×10^{-10}	480	0.271	0.117	0.127	$3.73 \cdot 10^{-4}$	$0.867 \cdot 10^{-4}$	$3.41 \cdot 10^{-4}$	0.801×10^{-3}	$3.73 \cdot 10^9$	$3.31 \cdot 10^9$
5b	5.71	7.67	483	.410	.171	.127	3.36	.965	6.47	1.08	3.28	2.83
5c	9.65	7.51	486	.650	.332	.124	2.71	1.19	10.9	1.48	2.64	2.71
5d	14.1	7.42	489	.976	.441	.123	2.07	1.25	16.8	2.01	3.08	2.82
5e	17.6	7.38	491	1.13	.509	.122	2.16	1.31	18.9	2.24	2.88	2.63
											Average k_i = $(3.12 \pm 0.30) \cdot 10^9$ ±10 percent	Average k_{ia} = $(2.86 \pm 0.22) \cdot 10^9$ ±8 percent
6a	3.04×10^{-10}	7.39×10^{-10}	500	0.259	0.069	0.122	3.26×10^{-4}	$0.582 \cdot 10^{-4}$	27.9×10^{-4}	$3.18 \cdot 10^{-3}$	$5.04 \cdot 10^9$	$3.36 \cdot 10^9$
6b	6.75	7.36	501	.608	.203	.122	2.57	.818	94.5	9.79	4.80	3.69
6c	10.1	7.19	503	.721	.261	.120	2.28	.863	108	11.1	3.71	2.98
6d	17.2	7.19	504	1.27	.449	.119	1.75	1.01	195	19.8	3.91	3.10
6e	21.3	7.04	506	1.52	.538	.117	1.51	1.01	210	21.2	3.86	3.05
											Average k_i = $(4.26 \pm 0.52) \cdot 10^9$ ±12 percent	Average k_{ia} = $(3.24 \pm 0.22) \cdot 10^9$ ±7 percent
7a	5.84×10^{-10}	6.76×10^{-10}	546	0.727	0.300	0.112	1.76×10^{-4}	0.630×10^{-4}	86.4×10^{-4}	$8.88 \cdot 10^{-3}$	$6.39 \cdot 10^9$	$5.56 \cdot 10^9$
7b	10.3	6.62	547	1.34	.512	.110	1.25	.692	147	14.9	7.20	5.93
7c	9.88	6.61	549	1.31	.466	.109	1.24	.633	140	14.2	7.68	6.06
											Average k_i = $(7.09 \pm 0.47) \cdot 10^9$ ±7 percent	Average k_{ia} = $(5.85 \pm 0.17) \cdot 10^9$ ±3 percent
8a	1.83×10^{-10}	6.70×10^{-10}	554	0.198	0.071	0.111	2.41×10^{-4}	0.360×10^{-4}	12.6×10^{-4}	1.54×10^{-3}	$6.18 \cdot 10^9$	4.88 4.88×10^9
8b	3.35	6.70	555	.445	.191	.111	2.01	.411	43.2	4.56	6.71	6.00
8c	7.18	6.77	556	.783	.327	.112	1.70	.626	96.1	9.84	5.55	4.88
8d	11.4	6.46	556	1.14	.468	.107	1.26	.620	115	11.7	5.41	4.67
											Average k_i = $(5.96 \pm 0.48) \cdot 10^9$ ±8 percent	Average k_{ia} = $(5.11 \pm 0.43) \cdot 10^9$ ±8 percent

TABLE II. - Concluded. RATE MEASUREMENT DATA FOR O + DCl REACTION

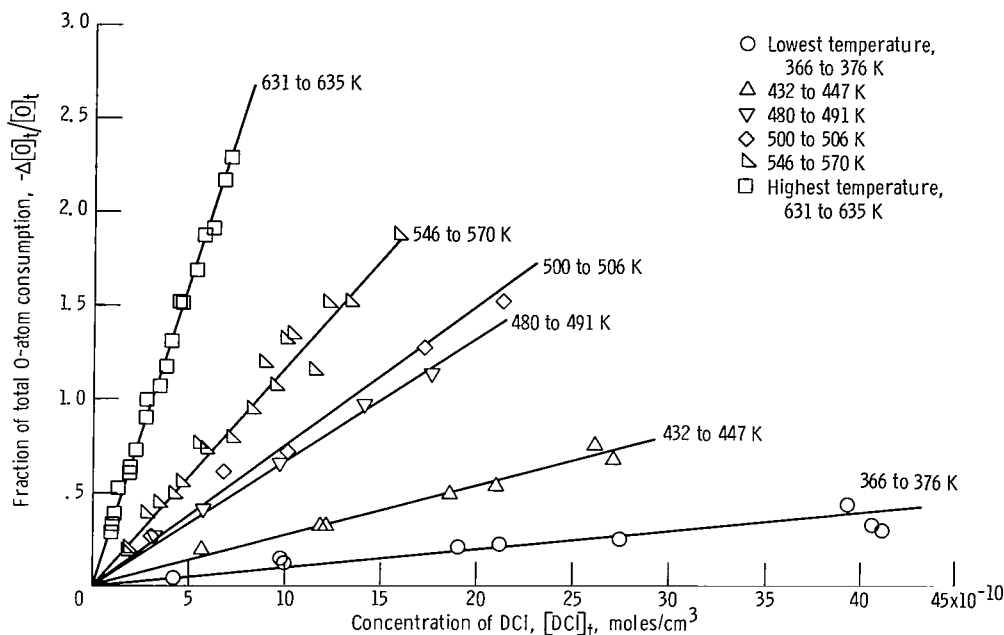| Run	Concentration of DCl at reaction time t, $[DCl]_t$, moles/cm^3	Initial O-atom concentration prior to reaction, $[O]_o$, moles/cm^3	Temperature, K	Fraction of total O-atom consumption, $-\dfrac{\Delta[O]_t}{[O]_t}$	O_2 produced due to added DCl, $\dfrac{\Delta[O_2]_t}{[O]_t}$	Residence, Δt, sec	$k_5 \Delta t[O]_t[M]$ A	$k_6 \Delta t[O_2]_t[M]$ B	$k_9 \Delta t[Cl_2]_t$ C	A + B + C	Rate constant, k_1, cm^3 mole^{-1} sec^{-1}	Rate constant, k_{1a}, cm^3 mole^{-1} sec^{-1}
9a	$1.72 \cdot 10^{-10}$	6.63×10^{-10}	560	0.190	0.062	0.110	2.35×10^{-4}	0.331×10^{-4}	$11.2 \cdot 10^{-4}$	$1.39 \cdot 10^{-3}$	$6.70 \cdot 10^9$	$5.03 \cdot 10^9$
9b	4.12	6.64	560	.480	.173	.110	1.92	.461	46.7	4.91	6.67	5.30
9c	8.23	6.51	561	.942	.438	.108	1.40	.625	98.1	10.0	5.56	5.30
9d	13.3	6.44	562	1.51	.581	.107	1.07	.630	147	14.9	6.44	5.32
											Average k_1 = $(6.34 \pm 0.40) \cdot 10^9$ ±6 percent	Average k_{1a} = $(5.24 \pm 0.13) \cdot 10^9$ ±2 percent
10a	$4.48 \cdot 10^{-10}$	$6.56 \cdot 10^{-10}$	565	0.553	0.258	0.107	$1.73 \cdot 10^{-4}$	$0.560 \cdot 10^{-4}$	53.5×10^{-4}	$5.58 \cdot 10^{-3}$	$6.04 \cdot 10^9$	$5.77 \cdot 10^9$
10b	9.36	6.42	566	1.06	.485	.105	1.25	.652	102	10.4	5.74	5.39
10c	15.8	6.38	567	1.86	.709	.104	.905	.665	161	16.2	6.92	5.67
10d	12.1	6.40	568	1.50	.683	.104	1.02	.698	136	13.8	6.45	5.95
											Average k_1 $(6.29 \pm 0.43) \cdot 10^9$ ±7 percent	Average k_{1a} $(5.70 \pm 0.18) \cdot 10^9$ ±3 percent
11a	$2.70 \cdot 10^{-10}$	$6.49 \cdot 10^{-10}$	569	0.393	0.152	0.108	$1.99 \cdot 10^{-4}$	$0.351 \cdot 10^{-4}$	$33.8 \cdot 10^{-4}$	$3.62 \cdot 10^{-3}$	$8.13 \cdot 10^9$	$6.75 \cdot 10^9$
11b	5.44	6.49	569	.745	.273	.106	1.58	469	74.2	7.62	8.05	6.47
11c	8.79	6.38	570	1.18	.438	.104	1.21	.522	110	11.2	8.00	6.46
											Average k_1 $(8.06 \pm 0.05) \cdot 10^9$ ±1 percent	Average k_{1a} $(6.56 \pm 0.13) \cdot 10^9$ ±2 percent
12a	$1.33 \cdot 10^{-10}$	$5.53 \cdot 10^{-10}$	635	0.518	0.247	0.096	$1.11 \cdot 10^{-4}$	$0.305 \cdot 10^{-4}$	$28.2 \cdot 10^{-4}$	$2.96 \cdot 10^{-3}$	$2.11 \cdot 10^{10}$	$2.04 \cdot 10^{10}$
12b	2.74	5.51	634	.988	.438	.095	.842	.362	57.2	5.84	2.04	1.85
12c	4.02	5.48	633	1.31	.612	.095	.720	.401	73.7	7.48	1.82	1.73
12d	6.16	5.49	633	1.91	.809	.095	.583	.423	100	10.1	1.87	1.64
											Average k_1 $(1.96 \pm 0.10) \cdot 10^{10}$ ±5 percent	Average k_{1a} $(1.82 \pm 0.15) \cdot 10^{10}$ ±8 percent
13a	$0.97 \cdot 10^{-10}$	$5.58 \cdot 10^{-10}$	631	0.333	0.140	0.096	$1.29 \cdot 10^{-4}$	$0.259 \cdot 10^{-4}$	$15.1 \cdot 10^{-4}$	$1.68 \cdot 10^{-3}$	$2.06 \cdot 10^{10}$	$1.79 \cdot 10^{10}$
13b	1.94	5.55	631	.631	.278	.096	1.05	.322	36.1	3.75	1.88	1.70
13c	2.68	5.52	632	.898	368	.095	888	339	52.1	5.34	2.05	1.75
13d	4.58	5.54	632	1.51	.579	.096	688	.379	87.5	8.85	2.11	1.73
13e	4.43	5.53	633	1.52	.517	.096	.682	353	88.0	8.90	2.34	1.79
											Average k_1 $(2.09 \pm 0.08) \cdot 10^{10}$ 4 percent	Average k_{1a} $(1.75 \pm 0.03) \cdot 10^{10}$ 2 percent
14a	$0.905 \cdot 10^{-10}$	$5.56 \cdot 10^{-10}$	633	0.297	0.119	0.096	$1.32 \cdot 10^{-4}$	$0.246 \cdot 10^{-4}$	$12.5 \cdot 10^{-4}$	$1.41 \cdot 10^{-3}$	$2.03 \cdot 10^{10}$	$1.71 \cdot 10^{10}$
14b	1.96	5.53		.603	.244	096	1.06	.301	33.6	3.50	1.90	1.62
14c	3.39	5.49		1.07	.402	.095	.805	.336	61.4	6 26	2.06	1.67
14d	5.44	5.51		1.68	.648	.095	.635	.386	92.0	9.30	1.98	1.63
14e	6.82	5.51		2.16	.802	.095	.540	.400	109	11.0	2.08	1.67
											Average k_1 $(2.01 \pm 0.06) \cdot 10^{10}$ ±3 percent	Average k_{1a} $(1.66 \pm 0.03) \cdot 10^{10}$ ±2 percent
15a	$1.12 \cdot 10^{-10}$	$5.57 \cdot 10^{-10}$	632	0.388	0.161	0.096	$1.24 \cdot 10^{-4}$	$0.270 \cdot 10^{-4}$	$19.0 \cdot 10^{-4}$	$2.05 \cdot 10^{-3}$	$2.10 \cdot 10^{10}$	$1.81 \cdot 10^{10}$
15b	2.18	5.54	631	.727	.303	.096	.991	.275	42.4	4.37	2.01	1.74
15c	3.77	5.57	631	1.17	.455	.096	.801	.360	71.0	7.22	1.95	1.61
15d	5.71	5.51	632	1.87	.714	.095	.592	.395	99.6	10.1	2.11	1.72
15e	7.13	5.47	632	2.28	.818	.095	.515	.391	112	11.2	2.16	1.70
											Average k_1 $(2.07 \pm 0.07) \cdot 10^{10}$ ±3 percent	Average k_{1a} $(1.72 \pm 0.05) \cdot 10^{10}$ ±3 percent

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Figure 5. - O-atom consumption for O + DCl reaction.

Production of O_2 in the O + HCl and O + DCl Reactions

Before k_1 or k_i can be evaluated, the total O-atom consumed must be corrected for that portion contributed by subsequent reactions (2), (5), (6), (7), (9), and (10). Since most of this correction is represented by reaction (2), or the term $\Delta[O_2]_t/[O]_t$ in equation (22), $\Delta[O_2]_t$ was measured simultaneously with the O-atom consumed when HCl or DCl was added. These data are listed as $\Delta[O_2]_t/[O]_t$ in tables I and II. A plot of $\Delta[O_2]_t/[O]_t$ against $[HCl]_t$ is shown in figure 6. Scatter of this data is about 10 percent and is slightly poorer than the O-atom consumption data for HCl. A comparison of this figure with figure 4 (O-atom consumption against $[HCl]_t$) showed that this correction was about 50 to 55 percent at the lowest temperature and about 35 to 40 percent for the higher temperatures.

The data for the O_2 production due to added DCl are shown in figure 7. The scatter of this data was also slightly more than that for the O-atom-consumed data for DCl. A comparison of this figure with that for the $-\Delta[O]_t/[O]_t$ against $[DCl]_t$ plot of figure 5 showed that this correction was about 30 to 40 percent for the entire temperature range.

Rate Constants for the O + HCl Reaction

The rate constants k_1 and k_{1a} for the O + HCl reaction were calculated using
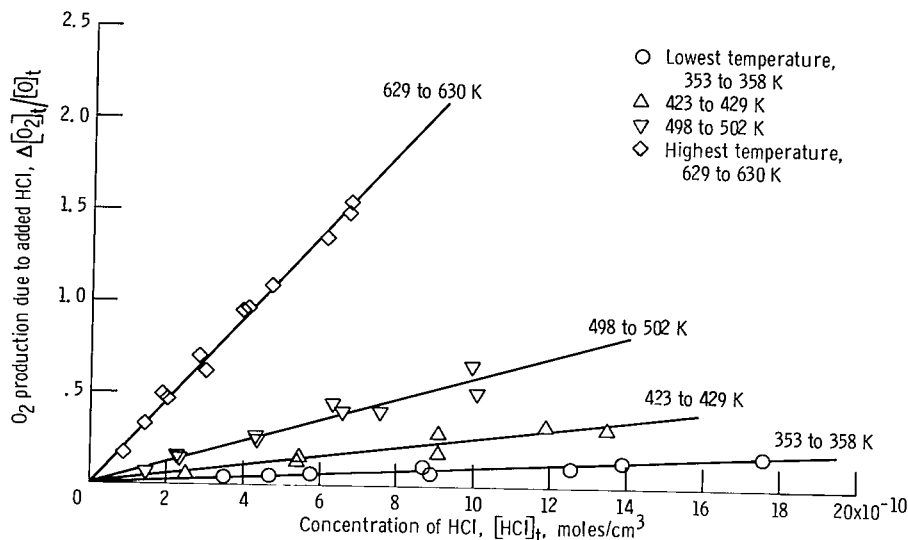
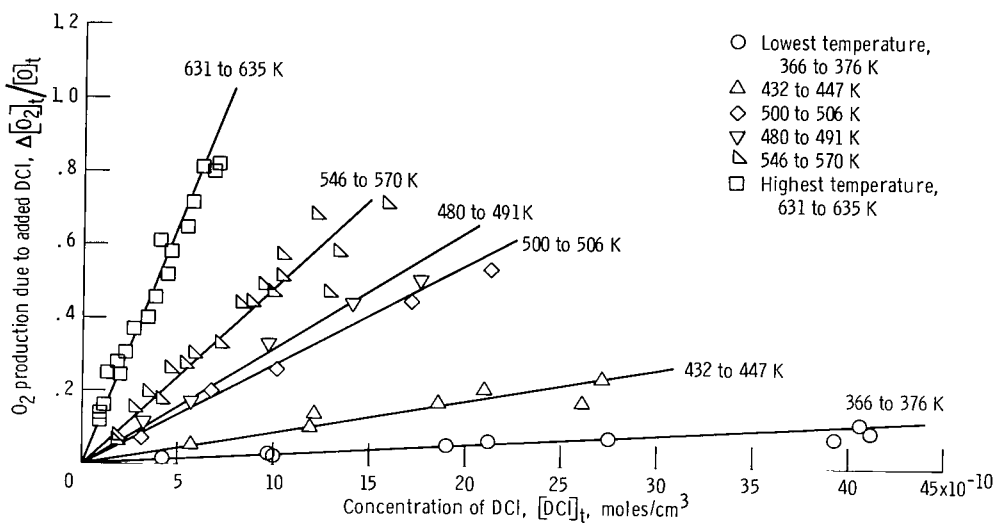Figure 6. - O_2 production for O + HCl reaction.

Figure 7. - O_2 production for O + DCl reaction.

equations (15) and (22), and these results are tabulated in table I. For the k_1 calculation the correction to the total O-atom consumed represented by the following three terms: (1) $k_5 \Delta t[O]_t[M]$, (2) $k_6 \Delta t[O_2]_t[M]$, and (3) $k_9 \Delta t[Cl_2]_t$ is a small one. For the O + HCl reaction this correction, designated as Ⓐ+Ⓑ+Ⓒ in table I, amounted to about a 7-percent correction to k_1 at the lowest temperature and decreased to less than a 2-percent correction at the higher temperatures. The average deviations in k_1 values are listed for the four temperatures. The average k_1 values varied from about ±16 percent at the lowest temperature to about ±10 percent or less for the three higher temperatures.
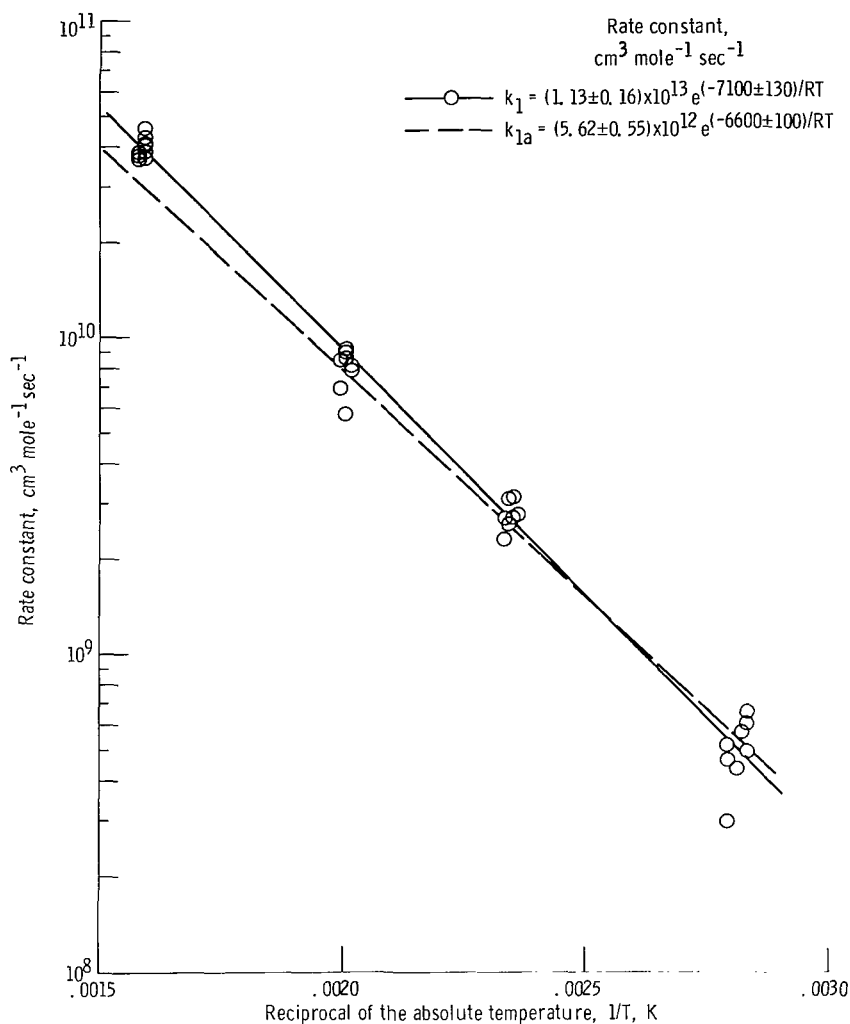
Figure 8. - Rate constant for O + HCl reaction: $O + HCl \xrightarrow{k_1, k_{1a}} OH + Cl$.

An Arrhenius plot of $\log k_1$ against the reciprocal of the absolute temperature $1/T$ (in K) is shown in figure 8. A least-squares line through all the data shown in figure 8 yielded a rate constant $k_1 = (1.13 \pm 0.16) \times 10^{13} \ e^{(-7100 \pm 130)/RT} \ cm^3 \ mole^{-1} \ sec^{-1}$. Error limits in the pre-exponential and activation energy are standard deviations. On the same figure the results of the k_{1a} calculation are shown plotted as a broken line. This line is the least-squares line determined by all the k_{1a} data listed in table I;

$k_{1a} = (5.62 \pm 0.55) \times 10^{12} \ e^{(-6600 \pm 100)/RT} \ cm^3 \ mole^{-1} \ sec^{-1}$. The difference between k_1 and k_{1a} is small so the assumptions of steady state for the OH radical and that all the O-atom were consumed by reactions (1) and (2) are good approximations. This also suggests that any errors in the calculation of the correction terms designated as (A) + (B) + (C) in equation (22) are small and do not appreciably affect k_1.
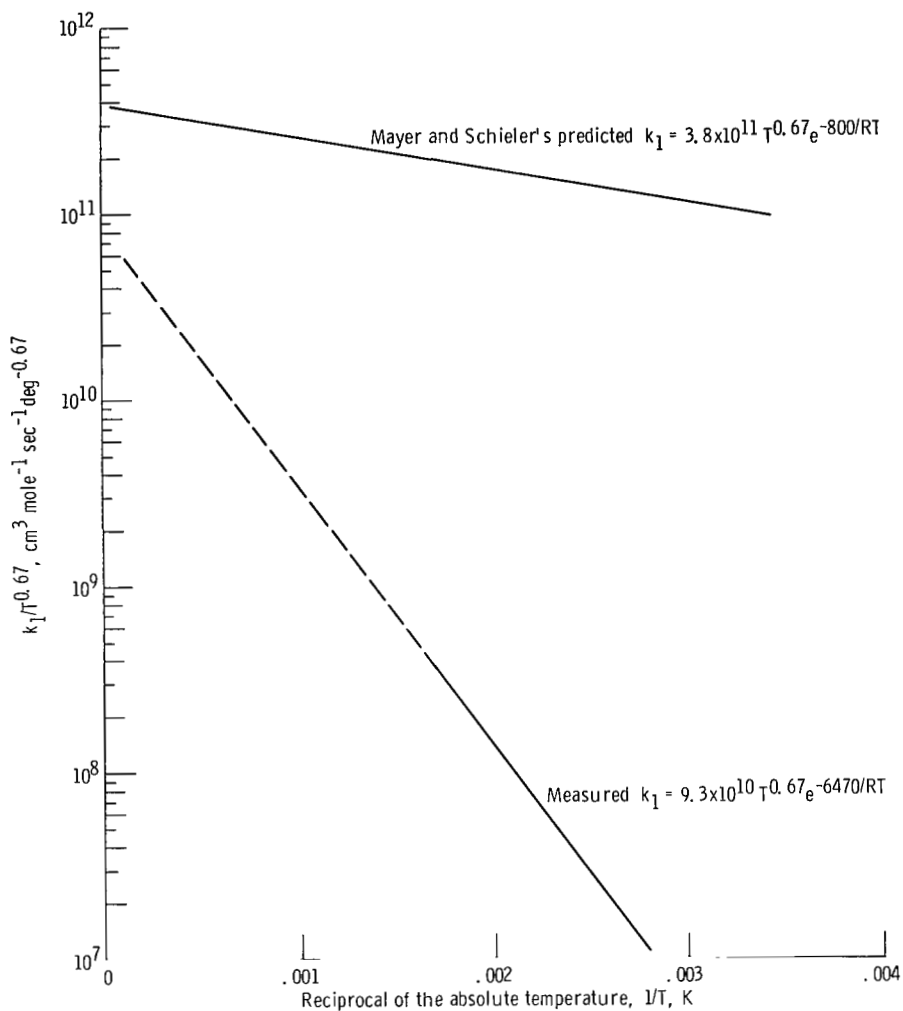
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Figure 9. – Comparison of experimental and predicted rate constant k_1.

In figure 9 our measured k_1 was replotted as $k_1/T^{0.67}$ against $1/T$ (in K) and compared with Mayer and Schieler's theoretical computed k_1 value of $3.8 \times 10^{11} T^{0.67} e^{-800/RT}$ (ref. 2). The measured k_1 is so much lower than the theoretical k_1 that it appears that this large discrepancy cannot be resolved on the basis of the Mayer-Schieler electron spin repulsion theory (ref. 13).

Rate Constants for the O + DCl Reaction

The results of the k_i and k_{ia} calculation for the O + DCl reaction are listed in table II. For the k_i calculation the correction to the total O-atom consumption, designated as (A) + (B) + (C) in table II, amounted to a correction of about 2 percent or
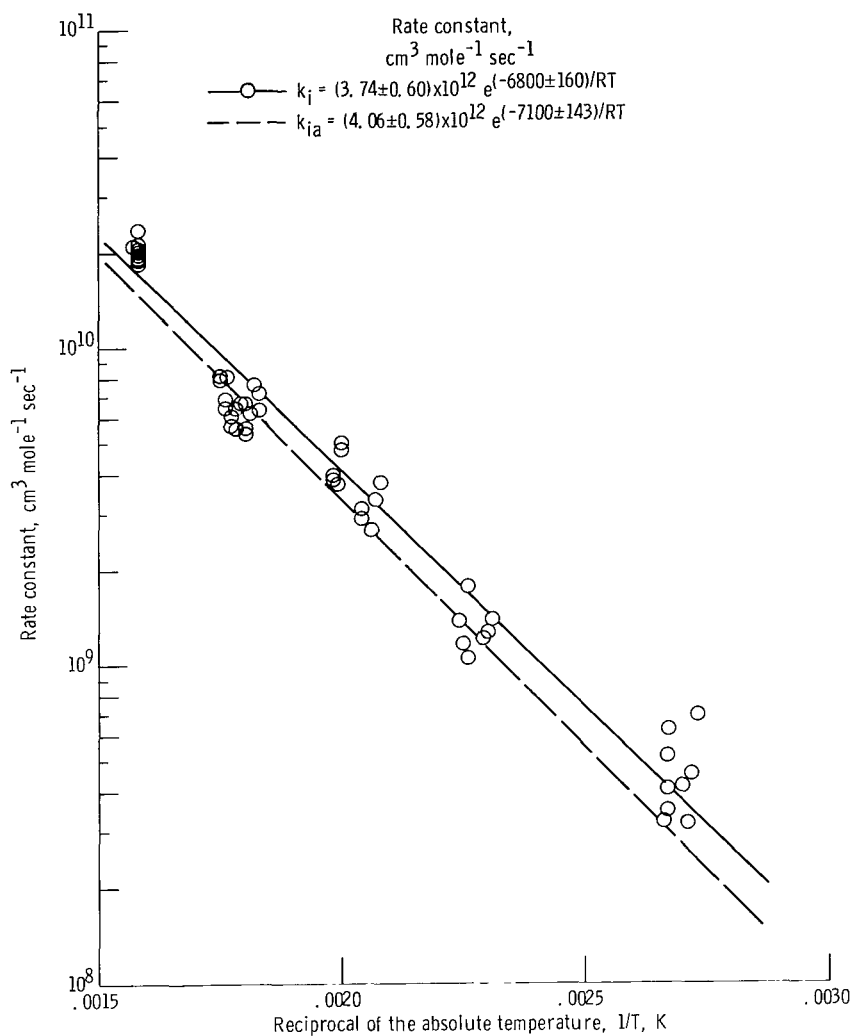
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Figure 10. - Rate constant for O + DCl reaction: $O + DCl \xrightarrow{k_i, k_{ia}} OD + Cl$.

less to k_i for the entire temperature range. The average deviations in k_i values ranged from about ±24 percent at the lowest temperature to about ±3 percent at the highest temperature.

Figure 10 is an Arrhenius plot of all the k_i data. A least-squares line through all the data produced a rate constant $k_i = (3.74 \pm 0.60) \times 10^{12} \, e^{(-6800 \pm 170)/RT} \, cm^3 \, mole^{-1} \, sec^{-1}$, where the error limits are standard deviations. The k_{ia} results are plotted in figure 10 as a broken line; $k_{ia} = (4.06 \pm 0.58) \times 10^{12} \, e^{(-7100 \pm 143)/RT} \, cm^3 \, mole^{-1} \, sec^{-1}$. The difference between k_i and k_{ia} is also small so that the assumptions of steady state for the OD radical and that all the O-atoms were consumed by reactions corresponding to reactions (1) and (2) are good approximations for the O + DCl reaction also. This again suggests that any errors in the calculation of the correction terms -

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$\textcircled{A} + \textcircled{B} + \textcircled{C}$ - in the corresponding expression for k_i are small and do not affect appreciably k_i.

Comparison of k_1 and k_i

For the temperature range investigated, k_1 values were about twice those for k_i. This result is in qualitative agreement with the theory which suggests that for reactants such as HCl and DCl, in which the isotopic atom is chemically bound, the lighter molecule will have a larger rate constant (ref. 14).

The difference in the measured activation energy between k_1 and k_i of 1250 joules per mole (300 cal/mole) is just within the experimental error limit; therefore, it is difficult to decide whether this is a real difference. On the theoretical basis that the difference in activation energy between two isotopic forms of a molecule may be attributed to the difference in their zero-point energies, a higher activation energy would be predicted for k_i. In view of the indicated uncertainty in our measurements of activation energy, any actual difference in the activation energy between k_1 and k_i is probably a small one.

SUMMARY OF RESULTS

Kinetic rate measurements for the O + HCl and O + DCl reactions were made and the results were as follows:

1. For the O + HCl reaction, the reaction products were Cl-atom, O_2, H_2, some H_2O, and a trace of Cl_2. H_2O was a reaction product only at relatively higher ratios of $[HCl]_t/[O]_t$ and at the higher temperatures. The rate constant was found to be $(1.13 \pm 0.16) \times 10^{13} e^{(-7100 \pm 130)/RT}$ cm^3 $mole^{-1}$ sec^{-1}. The measured activation energy was about eight times the value predicted by Mayer and Schieler.

2. For the corresponding reaction O + DCl $\longrightarrow$ OD + Cl, the rate constant was found to be $(3.74 \pm 0.60) \times 10^{12} e^{(-6800 \pm 170)/RT}$ cm^3 $mole^{-1}$ sec^{-1}.

3. A comparison of k_1 with k_i for the temperatures investigated showed that k_1 values were about twice those for k_i. That the difference in the measured activation energy of 1250 joules per mole (300 cal/mole) was within the experimental uncertainty indicated that any actual difference in activation energy between k_1 and k_i is a small one.

4. On the basis of the H_2O produced in the O + HCl reaction, an activation energy of about 21 000 joules per mole (5000 cal/mole) was obtained for the

OH + HCl→H_2O + Cl reaction. This value can be compared with the estimated value of 27 000 joules per mole (6500 cal/mole) in the literature.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, June 2, 1971,
129-01.

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