

Reactions of Chlorine Oxide Radicals

Part 3.—Kinetics of the Decay Reaction of the ClO($X^2\Pi$) Radical

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The kinetics of the decay reaction of the ClO($X^2\Pi$) radical have been investigated by time-resolved electronic absorption spectrophotometry in a discharge-flow system. Ar and Ar+SF₆ mixtures were used as carrier gases at 294 K; over the concentration range $45.31 \times 10^{-8} > [\text{Ar}] > 2.53 \times 10^{-8}$ g atom cm⁻³ the decay reaction of ClO radicals was second order. Insignificant effects of third bodies (M = Ar, SF₆) were observed. Decay of ClO occurred predominantly under these conditions via reaction (2),

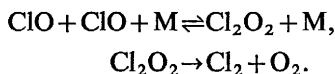


with $k_2 = 10^{(11.89 \pm 0.04)} \exp [(-1150 \pm 50)/T] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in the temperature range 273 to 710 K. The low activation energy for reaction (2) and the large range of T^{-1} of these measurements closely define the frequency factor for reaction (2).

The data were combined with earlier measurements of k_{-2} by Johnston, Morris and Van den Bogaerde to give an accurate value for the dissociation energy of the ClOO radical,

$$D_{298}^\circ(\text{Cl}-\text{OO}) = (29 \pm 3) \text{ kJ mol}^{-1}.$$

The rate of second order decay of ClO($X^2\Pi$) radicals has recently been investigated¹ using electronic absorption spectrophotometry in a discharge flow system at total pressures (of Ar or a mixture of Ar with N₂ or O₂) between 110 and 400 N m⁻² and from 294 to 495 K. Evidence was obtained¹ that this reaction occurs by means of a simple bimolecular step, forming a Cl atom and an unstable ClOO peroxy radical, which may then either dissociate to Cl+O₂, or may react with Cl, forming Cl₂+O₂. A later study by Johnston, Morris and Van den Bogaerde (JMV)² of the photochemical reaction between Cl₂ and O₂ at 298 K using molecular modulation spectrometry has provided additional evidence for this mechanism for the decay of ClO in the 10²-10³ N m⁻² total pressure region. In the work cited,² the gaseous intermediate ClOO was detected for the first time by means of its electronic and vibrational absorption spectra, and the ultraviolet spectrum of ClO was also observed. The measurements of JMV were carried out at higher pressures (7-100 kN m⁻²) than those of the discharge flow studies,¹ using O₂ or Ar as inert gas M. Under these conditions, the rate of decay of ClO radicals was found to be overall third order,²—second order in [ClO], and first order in [M], and the following mechanism, earlier put forward¹ to reconcile discharge flow work with flash photolysis studies, was proposed;



In the present work, the second order rate constant for ClO decay has been measured over a much wider range of Ar pressures than in earlier work,¹ and for SF₆ as inert gas. Under these conditions, we could not detect any major contribution to removal of ClO radicals from the "high pressure" third order reaction of JMV forming Cl₂O₂. It appears that the total pressure of argon at which second and third

order reactions contribute equally to removal of ClO is considerably greater than that tentatively suggested by JMV. The results of both studies (that of JMV and of ourselves) are nevertheless consistent with one another if the earlier estimate of $D_{298}^0(\text{Cl}-\text{OO})$ is revised by a few kJ mol^{-1} .

EXPERIMENTAL

THE FLOW SYSTEM

Linear velocities up to 10 m s^{-1} at 200 N m^{-2} of argon in a 28 mm i.d. Pyrex or silica flow tube were obtained using a single-stage 5 l. s^{-1} rotary pump connected via two high conductance triple-surface cold traps and a 25 mm stopcock. Upstream of the flow tube was a silica discharge tube, in which dilute mixtures of dry Cl_2 (1-10 mol %) with dry Ar were partially dissociated by means of an air-cooled microwave discharge (40-80 W at 2450 MHz). The discharge tube (although not the flow tube) was treated with 10 % phosphoric acid, and excess water was pumped off under vacuum with a 77 K cold trap for 1 h in order to produce a coating of phosphoric acid exerting a negligible vapour pressure of water. Such phosphoric acid coated discharges produce stable concentrations of Cl atoms ($[\text{Cl}] < 2 \times 10^{-9} \text{ g atom cm}^{-3}$).

In all cases, a variant of the fixed observation point method was used for kinetic analysis. In this method, a pair of Spectrosil windows, cemented onto the flow tube and flush with the sides of the tube in order to avoid dead volume, constituted the observation point (fig. 1). Absorption intensities by ClO radicals were measured at this point normal to the flow axis. In the first (Pyrex) flow tube used, a series of four identical inlet jets were provided at equal intervals along the tube axis upstream of the observation point. By addition of the same flow of chlorine dioxide to (an excess of) Cl atoms at each of these four jets in turn, four different times of reaction between the jets and the observation point were obtained. This flow tube, and the glass inlet leads, were enclosed in an electric furnace insulated with Triton ceramic wool blanket (A. D. Wood), which was found superior to asbestos string. The Pyrex tube was used for measurements of decay rates of ClO up to 550 K, above which temperature premature spontaneous decomposition of chlorine dioxide in the inlet leads was found to occur.¹ This decomposition was manifested as a sudden propagation back from an inlet jet of a visible yellow-orange flame front; the flame front was fortunately arrested at the metal needle valve used to control the flow of OClO.

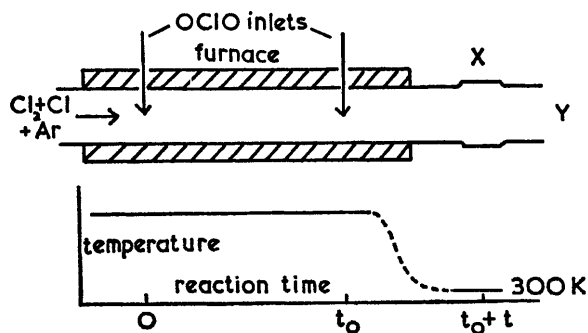


FIG. 1.—Flow system used for study of decay reaction of ClO radicals. X, fixed observation point; Spectrosil windows for spectrophotometric measurements. Y, to pump.

For studies at temperatures between 550 K and 710 K, a flow tube of similar dimensions was constructed from silica (Vitreosil), and at the same time the opportunity was taken to redesign the OClO inlet. Replacing the 4 mm bore inlet tubes by silica tubing having twin 1 mm bores caused the velocity of the incoming OClO to exceed that of the backward-travelling flame front, and premature decomposition of OClO was thus inhibited up to 710 K. In order to vary the reaction time, the inlet tube was traversed along the major axis of the flow tube via a water-cooled O-ring collet seal; a small disc diffuser was fitted to the end of the inlet tube to promote rapid mixing of OClO.

MEASUREMENT OF ABSORPTION INTENSITIES BY ClO RADICALS

The optical system for absorption measurements was based on that described previously (see fig. 2 of ref. 3). A four traversal (14 cm) path length with White optics was used for absorption by ClO radicals of continuum radiation from a deuterium arc lamp; the transmitted radiation was dispersed by an Optica CF4 grating monochromator and detected with an EMI 9558 QB photomultiplier. After amplification in a low-noise picoammeter, 90 to 99 % of the D.C. component of the output signal was backed off potentiometrically and the remaining 1 to 10 % displayed as full scale on a 25 cm chart recorder. At the EHT voltages used (~ 800 V), the photomultiplier dark current and its fluctuations were negligible compared to the photocurrent; using a 2 s time constant the peak-to-peak random noise associated with the latter was equivalent to $\sim \pm 0.1$ % of absorption. D.C. signals and associated noise were recorded for ~ 50 s and integrated from the chart, so that the final random error in absorbance measurements was $\sim \pm 0.02$ %. No problems of long-term drift attributable to the deuterium lamp or electronic equipment were encountered. The optical system, which was sensitive to mechanical vibration, was clamped independently of the vacuum system. Absorption intensities were measured using the (12,0) band head of the $A^2\Pi_{3/2} - X^2\Pi_{3/2}$ system of ClO at 277.2 nm, and were converted to equivalent absorption intensities in the continuum at 257.7 nm, employing the measured ratio of absorption cross-sections σ .¹ Absolute concentrations of ClO were then calculated using Beer's Law and the previously determined¹ value of $\sigma = (4.8 \pm 0.1) \times 10^{-22}$ m² at 257.7 nm and 298 K.

REAGENTS

Chlorine, argon and sulphur hexafluoride were dried samples of the best available cylinder gases. Chlorine dioxide was prepared by heating a mixture of oxalic acid and potassium chlorate in an armoured fume cupboard.¹ The dry product was distilled from a 193 K trap into three 5 l. bulbs and then diluted with argon. The only major mass peaks (other than Ar⁺, Ar²⁺) shown by analysis with an E.A.I. Quad 150 Å mass spectrometer, were those characteristic of OClO (m/e 69, 67, 53, 51), indicating >95 % purity. Traces of H₂O and CO₂ were observed; Cl₂ was absent in freshly prepared material but after a few days standing up to 10 % of Cl₂ was found to be produced by slow decomposition of chlorine dioxide.

A conventional vacuum line was used for storage and metering of reagents. Capillary flow meters with DC 704 silicone oil (Ar, OClO, SF₆) or H₂SO₄(Cl₂) manometers were used to measure the flow rates of reagents, which were controlled with brass, monel, stainless steel or Teflon needle valves.

ERRORS

The range of flow system parameters used for this kinetic study was typical of flow tube kinetic investigations, as has been indicated above, except that the maximum range of total pressures used was compatible with the one-dimensional plug flow approximation. Values for the dimensionless parameters u , B^2 and δ were used as criteria for this approximation, as suggested by Walker.⁴ Neglect of radial and axial concentration gradients was also confirmed by the order-of-magnitude criteria of Kaufman.⁵

Poiseuille pressure gradients were calculated to be <5 % over the length of the reaction flow tube. Concentrations of atoms and radicals were <5 % of argon concentration in order to ensure essentially isothermal reaction conditions.

RESULTS

PRODUCTION OF ClO ($X^2\Pi$, $v'' = 0$) RADICALS

The reaction between chlorine dioxide and a stoichiometric excess of ground state Cl($^2P_{3/2}$) atoms, generated by a microwave discharge in Cl₂ + Ar mixtures, was used to generate ClO($X^2\Pi_{3/2}$, $v'' = 0$) radicals¹:



The ClO radical was detected by means of its intense electronic band absorption system between 260 and 280 nm, and concentrations of ClO were measured spectrophotometrically as described above.

KINETICS OF DECAY OF ClO RADICALS USING THE FIXED OBSERVATION POINT METHOD

In earlier work, we have determined the second order rate constant k for decay of ClO radicals by spectrophotometric measurements of [ClO] along the length of a rectangular silica flow tube, using a travelling monochromator + optical bench assembly.¹ For work at temperatures above 300 K, a furnace was wound on this tube with observation ports in the windings at intervals along the tube to allow optical measurements. Corrections were applied for the slight temperature decreases inevitable in the region of the observation ports, and for the decrease in σ with increase of temperature.¹

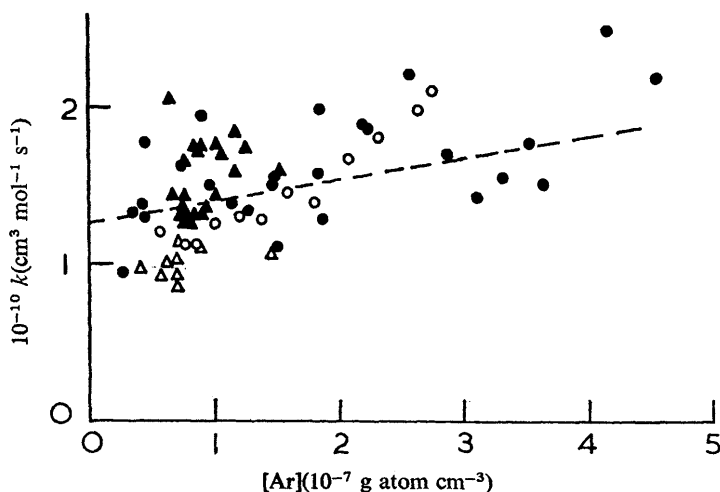


FIG. 2.—Measurement of second-order decay rate constant k at 293 K for argon third body over the concentration range $2.53 \times 10^{-8} \leq [\text{Ar}] \leq 45.31 \times 10^{-8} \text{ g atom cm}^{-3}$. ● this work; ▲ ref. 1(a); ○ ref. 6.

The fixed observation point method has been shown to be valuable in the analyses of the kinetics of pseudo first order reactions in discharge flow systems. It is shown in this work that this method, which has important advantages especially for measurements at elevated temperatures, can be applied to second order decay of ClO radicals. A constant concentration of ClO radicals was generated by addition of a constant concentration of OClO to an excess of chlorine atoms, and use of the sliding OClO inlet enabled the time of residence of ClO radicals to be varied between the inlet and a fixed observation point. A simple second order analysis then holds for the decay of ClO,

$$[\text{ClO}]^{-1} = [\text{ClO}]_0^{-1} + kt.$$

Plots of $[\text{ClO}]^{-1}$ against t were linear, as expected, with slopes k , independent of $[\text{ClO}]_0$ over a five-fold concentration range. Fig. 2 shows the results of 26 determinations of k at 293 K in argon carrier gas in the concentration range $2.53 \times 10^{-8} \leq [\text{Ar}] \leq 45.31 \times 10^{-8} \text{ g atom cm}^{-3}$ (60 to 1100 N m⁻²). The mean value in argon carrier gas

was $k = (1.64 \pm 0.25) \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 293 K. As shown in fig. 2, this value is in good agreement (within random error) with two previous determinations over a limited range of $[\text{Ar}]$ (ref. 1) and with a third recent determination,⁶ all using different experimental systems and independently-calibrated flowmeters, and all using the travelling monochromator method referred to above. A least mean squares line on the data of fig. 2 showed a positive slope, but its magnitude was within the limits of error of a zero slope.

In order to investigate further the possible effects of third body M upon k_2 , some of the Ar carrier gas used for the decay experiments was replaced by the dense inert gas SF_6 . The mean value of twenty measurements of k in a carrier gas containing 35 mol % of SF_6 was $(1.73 \pm 0.25) \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 294 K and over the range $5.75 \times 10^{-8} \leq ([\text{Ar}] + [\text{SF}_6]) \leq 24.10 \times 10^{-8} \text{ mol cm}^{-3}$. As for $[\text{Ar}]$, no significant dependence of k upon $[\text{M}]$ was observed in this range. Table 1 shows the data.

TABLE 1.—VALUES FOR k IN $\text{Ar} + \text{SF}_6$ INERT CARRIER GAS AT 294 K

mol fraction of $\text{SF}_6 = 0.35$			
$10^{-10} k$ ($\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	$10^8 ([\text{Ar}] + [\text{SF}_6])$ (mol cm^{-3})	$10^{-10} k$ ($\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	$10^8 ([\text{Ar}] + [\text{SF}_6])$ (mol cm^{-3})
2.18	5.75	1.71	15.72
0.74	6.23	2.19	16.16
1.92	7.90	1.34	17.70
2.02	7.99	1.71	18.17
1.62	9.27	1.50	18.98
2.49	9.44	2.03	19.67
1.26	10.63	1.77	22.01
1.74	12.78	1.81	22.48
1.41	13.17	1.78	23.36
1.63	14.54	1.81	24.10

DETERMINATION OF k AT ELEVATED TEMPERATURES

The fixed observation point with constant initial $[\text{ClO}]_0$ was used for measurements of k in a heated tube at temperature T_1 ; the concentration of ClO remaining after various times ($t_0 + t$) was measured downstream from the end of the furnace windings at 293 K, t is the minimum time of residence between the sliding inlet and the observation point (fig. 1). The eqn (1) holds,

$$[\text{ClO}]^{-1} = [\text{ClO}]_0^{-1} + kt_0 + \int_{t_0}^{(t_0+t)} k(T) dt \quad (1)$$

The integral is not accurately known, since k is a function of T , and T does not fall to 293 K immediately after the furnace windings. It may be eliminated from eqn (1), however, by variation of t_0 , as in the fixed observation point method; plots of $[\text{ClO}]^{-1}$ are thus expected to be linear, with slopes equal to k (at temperature T_1). It should be noted that this method, which enables absorption intensities to be measured at ambient temperature, avoids problems of heat loss from windows in the furnace wall, and the necessity for determination of the absorption cross-section of ClO at each elevated temperature employed.

The heterogeneous decay of $\text{Cl}(^2P_{3/2})$ atoms at the walls of an uncoated or H_3PO_4 -coated Pyrex or silica tube becomes considerable at temperatures above 350 K. Rapid decay of $[\text{Cl}]$ would be very troublesome in the fixed observation point method, since it would prove difficult or impossible to ensure a stoichiometric excess of Cl over OClO and hence constant $[\text{ClO}]_0$, all the way down a heated tube. Fortunately, it was found earlier and confirmed here, that passage, for a short while, of chlorine

dioxide and chlorine atoms through an uncoated Pyrex or silica tube, caused a drastic reduction in the heterogeneous decay of Cl atoms. It was thus possible to measure k at fifteen temperatures between 273 and 710 K using the fixed observation point

TABLE 2.—VARIATION OF k AND k_2 ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$) WITH TEMPERATURE
 $k = k_2 + k_{3,\text{Ar}}[\text{Ar}]$ (see text)

T (K)	$10^{-10} k$		$10^{-10} k_2$	
	this work	ref. 1	this work	ref. 1
273	1.4 ₃		1.2 ₃	
293	1.6 ₄		1.4 ₅	
294		1.2 ₀		1.1 ₀
312	1.8 ₆		1.6 ₈	
318		1.5 ₀		1.4 ₁
330	1.9 ₃		1.7 ₆	
332	2.1 ₁		1.9 ₄	
342	2.3 ₁	1.9 ₅	2.1 ₅	1.7 ₈
347	2.8 ₅		2.6 ₉	
357		1.8 ₂		1.7 ₅
369	3.5 ₈		3.4 ₃	
380		2.3 ₈		2.3 ₁
406		3.9 ₂		3.8 ₅
413	4.4 ₉		4.3 ₅	
442		3.7 ₅		3.6 ₉
444	6.2 ₁		6.0 ₈	
472		8.4 ₂		8.3 ₇
495		5.7 ₉		5.7 ₄
501	7.7 ₇		7.6 ₆	
550	8.8 ₁		8.7 ₁	
577	9.6 ₆		9.5 ₇	
675	14.2		14.1	
710	17.0		16.9	

method. (The upper temperature limit was determined by melting of the Viton O-ring used to seal the sliding inlet, and by the spontaneous decomposition of OClO which became difficult to suppress above 700 K).

Table 2 shows the present results for k which are in good agreement with earlier, less accurate data.¹

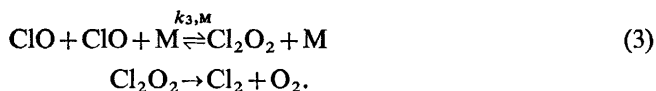
DISCUSSION

MECHANISM OF THE DECAY REACTION OF ClO RADICALS AT 298 K

Previous work on the ClO decay reaction in low pressures of Ar ($\sim 10^2 \text{ N m}^{-2}$)¹ and in high pressures of O₂ ($\sim 10^4 \text{ N m}^{-2}$) (ref. 2) has indicated the existence of two parallel paths for this decay process at 300 K: reaction (2), leading to Cl atoms,



and reaction (3), involving a third body M, and leading to Cl₂ + O₂:



ClO radicals decay by means of the second order mechanism (2) at sufficiently low

pressures, whilst with an increase in total pressure, reaction (3) gradually becomes predominant in rate. In this way, it is possible to reconcile the data of ref. 1 and 2, and also to some extent, earlier results of Porter and Wright ⁷ (see ref. 1 and 2 for discussion of this and other earlier work).

There has remained the problem that the value for k_2 calculated from the high pressure data of JMV is a factor of 4 less than that found directly at pressures near 200 N m⁻². This discrepancy could be due either to systematic errors in the calculation of k_2 by JMV, or to a significant dependence of second order decay rate constant k upon $[M]$ even at 200 N m⁻². We have attempted to resolve the difficulty by careful examination of possible third body effects upon k for $M = \text{Ar}$ and SF_6 , using a more accurate kinetic method than previously.

Plots of k against $[M]$, such as those of fig. 2 of this work, possess slopes equal to $k_{3,M}$ and intercepts equal to k_2 . A least mean squares line through the data of fig. 2 possesses a slope whose magnitude is greater than zero. However, this slope is within the limits of error of zero. In confirmation, no significant increase in k could be found consequent upon partial replacement of argon by sulphur hexafluoride as third body (table 1).

Any variation of k with $[M]$ ($M = \text{Ar}, \text{SF}_6$) in the range $2.5 \times 10^{-8} \leq [\text{Ar}] \leq 4.5 \times 10^{-7}$ g atom cm⁻³ is therefore of small magnitude. The small magnitude of the least mean squares slope $k_{3,\text{Ar}}$ is within the limits of error of JMV's direct determination, $k_{3,\text{Ar}} = 1.2 \times 10^{16}$ cm³ mol⁻² s⁻¹, which is shown by the broken line in fig. 2. Combining the value of $k_{3,\text{Ar}}$ from the data of JMV (based on five measurements in the range 50-700 Torr of argon) with the present values for k , k_2 is determined by a small correction ($\sim 10\%$), $k_2 = k - k_{3,\text{Ar}}[\text{Ar}]$ (see table 2). [It is noted that the values for k_2 thus found are insensitive to any unexpectedly large error in $k_{3,\text{Ar}}$]. The mean value for k_2 is $(1.45 \pm 0.1) \times 10^{10}$ cm³ mol⁻¹ s⁻¹ at 293 K which will be shown to correspond to $(1.51 \pm 0.1) \times 10^{10}$ cm³ mol⁻¹ s⁻¹ at 298 K.

As indicated above, these results for k_2 are quantitatively incompatible with the full analysis given by JMV, which leads to $k_2 = 3.8 \times 10^9$ cm³ mol⁻¹ s⁻¹. This low value for k_2 , and the value found for $k_{3,\text{Ar}}$, would give a large variation of k with $[\text{Ar}]$ in the 10^2 - 10^3 N m⁻² total pressure range, but no such variation was in fact observed. However, a reconciliation of the data is obtained if it is assumed that the dissociation energy of the radical ClOO is 3 kJ mol⁻¹ greater than the value estimated by JMV (26 kJ mol⁻¹). For the determination of k_2 , JMV combined their measured value for the rate constant k_{-2} of the reverse reaction,



with the equilibrium constant K_2 derived from a calculated ΔS_{298}° and an estimated ΔH_{298}° value. These thermodynamic parameters clearly depend upon the magnitude for S_{298}° and $\Delta H_{298(f)}^\circ$ of ClOO. Whilst the absolute entropy of ClOO can be calculated within close limits, the only estimates ¹⁻³ for the standard heat of formation of this radical are inferred from kinetic evidence. It appears to the writers that such estimates of $\Delta H_{298(f)}^\circ$ will have a probable error of about 10 kJ mol⁻¹.

It is therefore preferable to adopt the converse procedure to that of JMV: experimental values for k_2 from this work are combined with data for k_{-2} from JMV to determine K_2 . The magnitude of K_2 thus deduced at 298 K is 57. Taking the revised value ² of ΔS_{298}° for reaction (2) to be -10 J mol⁻¹ K⁻¹, a value is obtained for $\Delta H_{298(f)}^\circ$ (ClOO) of $(+93 \pm 2)$ kJ mol⁻¹ [$D_{298}^\circ(\text{ClOO}) = 29 \pm 3$ kJ mol⁻¹; $D_0^\circ(\text{ClOO}) = 25 \pm 3$ kJ mol⁻¹]. The error limits given are those of the uncertainty in $S_{298}^\circ(\text{ClOO})$ and the estimated experimental errors of k_2 and k_{-2} .

In this way, independent measurements of k_2 and k_{-2} are combined to give an accurate value for the dissociation energy of the ClOO radical. Modification of JMV's value for $\Delta H_{298(f)}^\circ(\text{ClOO})$, as described, then leads to the satisfactory conclusion that the present results and those of JMV can be integrated into the unified scheme of reactions and rate constants proposed earlier.²

VARIATION OF k_2 WITH TEMPERATURE

It has been shown that k_2 is related to the experimental second order rate constant for decay of ClO radicals, k by means of $k_2 = k - k_{3,M}[M]$, with $k_2 = (1.45 \pm 0.1) \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 293 K, and $k = (1.64 \pm 0.1) \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K. k possesses a significant activation energy ($\sim 10 \text{ kJ mol}^{-1}$), whilst k_3 is expected to show a small negative temperature coefficient.⁸ Hence, k/k_2 will converge to a value of unity as T increases, for a given range of $[M]$.

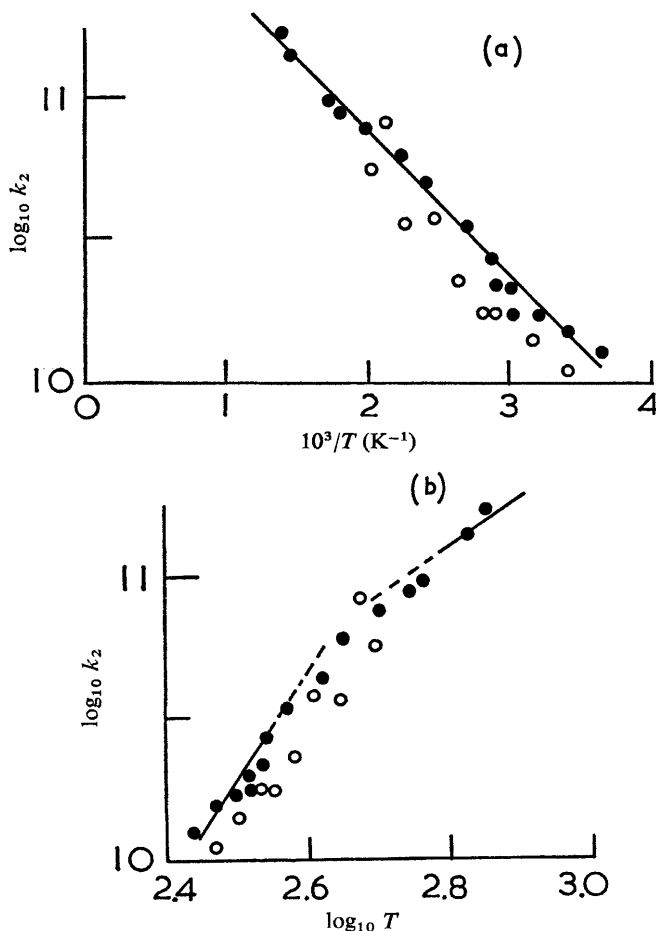


FIG. 3.—Variation of k_2 ($\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) with temperature. (a) Plot of $\log_{10} k_2$ against T^{-1} . (b) Plot of $\log_{10} k_2$ against $\log_{10} T$. ● this work; ○ ref. 1(b).

We have neglected any small temperature dependence of $k_{3,M}$ in correcting k to give k_2 in the range 273–710 K, since even at 293 K, the correction is only 10 %.

Table 2 shows the results for k_2 at various temperatures. The earlier data of Clyne and Coxon¹ for k have been similarly corrected for $k_3[M]$, and the resulting values for k_2 are in good agreement with the present work; fig. 3(a) shows all the data for k_2 in the Arrhenius form. The present data give

$$k_2 = (7.8 \pm 0.7) \times 10^{11} \exp [-(1150 \pm 50)/T] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ (273-710 K)},$$

in comparison with the corrected earlier data,¹

$$k_2 = (6 \pm 2) \times 10^{11} \exp [-(1200 \pm 150)/T] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ (294-495 K)}.$$

The wide range of T^{-1} over which measurements of k_2 have been made enabled the frequency factor to be deduced from an unusually short extrapolation.

Because of the low activation energy for k_2 ($9.6 \text{ kJ} = 2.3 \text{ kcal mol}^{-1}$), and the wide range of T^{-1} used for measurements of k_2 , the decay reaction $\text{ClO} + \text{ClO} \rightarrow \text{Cl} + \text{ClOO}$ should be a favourable case for attempting to isolate exponential and pre-exponential terms in the temperature function of a rate constant. Functions of the type,

$$k_2 = AT^n \exp (-E/RT),$$

were consequently examined for fit to the data, using computed values for k_2 at half-integral values of n . The best least mean squares fit was for $n = -\frac{1}{2}$,

$$k_2 = 3.14 \times 10^{13} T^{-\frac{1}{2}} \exp (-1420/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

However, the scatter of the data, even under the favourable conditions described above, was too great for the value of n to be defined to better than $\pm \frac{3}{2}$, giving the limits $+1 > n > -2$. The non-linearity of the log-log plot of fig. 3(b) indicates that a value for n appreciably outside these limits is improbable. The range of probable values for n lies within the ranges expected from simple models for the $\text{ClO} + \text{ClO}$ rate constants according to activated complex theory and collision theory.^{8, 9}

We thank Dr. G. S. Pearson for helpful discussion and the Ministry of Aviation Supply for a grant.

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(b) M. A. A. Clyne and J. A. Coxon, *Proc. Roy. Soc. A*, 1968, **303**, 207. Earlier work on the decay reactions of ClO is reviewed in these references and in ref. (2).

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⁵ F. Kaufman, *Prog. Reaction Kinetics*, 1961, **1**, 1.

⁶ M. A. A. Clyne and R. F. Walker, unpublished data.

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