i.e., in which the vibrationally hot S_4 molecule formed in reaction 10 is collisionally stabilized in the presence of excess inert gas.[27]

A brief study of the kinetics of S_2 recombination in the flash photolysis of CS_2 has been reported by Callear.[28] Because the S_2 buildup in the system was slow (about an order of magnitude slower than in our studies), it was permissible to neglect the finite length of flash duration and to arrive at an explicit formula for the time dependence of S_2 concentration (assuming that S_2 is formed by the recombination of S atoms). The formula correctly described the kinetics at a fixed pressure of inert gas (N_2) but was inadequate in describing the effect of pressure variation. This was attributed to complicating processes such as the reaction of atomic S with S_2 or higher sulfur polymers.

In a concurrent study of the flash photolysis of COS with kinetic mass spectrometry we verified the presence of large concentrations of S_6, along with some S_7 species in flashed COS. These observations require additional polymerization steps in the mechanism, *e.g.*

$$S_4 + S_4 \longrightarrow S_6 + S_2$$

$$S_4 + S_2 \longrightarrow S_6$$

$$S_2 + S_m \longrightarrow S_{m+2}$$

The observed second-order kinetics of the S_2 decay may be, therefore, to some extent fortuitous and the measured rate constant values should be regarded as upper limits for reaction 10.

Acknowledgments. The authors are thankful to Imperial Oil Limited and the National Research Council of Canada for financial support.

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(27) M. Eusuf and K. J. Laidler, *Trans. Faraday Soc.*, **59** 2750 (1963).
(28) A. B. Callear, *Proc. Roy Soc.* (London), **A276**, 401(1963).

Kinetic Study of the Reaction between Chlorine Dioxide and Potassium Iodide in Aqueous Solution

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Abstract: The rate of the reaction between chlorine dioxide and potassium iodide in aqueous solution was investigated spectrophotometrically by using a rapid-mixing syringe. Two distinctly different rates were observed in the pH range 5.5–8.5. The first reaction corresponds to the rapid formation of the intermediate $[ClO_2I^-]$. The second corresponds to the decomposition of the intermediate, which results in the formation of ClO_2^- and I_2. From the rate of the reaction as a function of temperature between 5 and 35°, activation enthalpies of 7.4 and 0.8 kcal/mole, respectively, were calculated for the two reactions.

The reactions and interactions of aqueous solutions of chlorine dioxide and sodium chlorite have recently been under investigation in this laboratory.[1–6] A common intermediate of the type $[Cl_2O_2]$ which can act either as an oxidizing or reducing agent[7] has been suggested.[8] The oxidation of iodide by chlorine dioxide was reported by Bray[9] where it was used in the analytical determination of chlorine dioxide. The purpose of this paper is to report on the intermediate formed in the reaction between chlorine dioxide and potassium iodide. This intermediate appears to have properties very similar to those reported for the $[Cl_2O_2]$ intermediate.

Experimental Section

All of the chemicals used were of analytical grade and were purified by techniques reported previously.[1,5,6] Chlorine dioxide was prepared from potassium chlorate and oxalic acid with the addition of small amounts of 4 *M* H_2SO_4.[3] The reaction was carried out in an all-Pyrex vessel which was shielded from light with aluminum foil. The liberated chlorine dioxide was passed through solutions of sodium carbonate to remove chlorine, hydrogen chloride, and carbon dioxide; the purified chlorine dioxide was collected in distilled water at ice temperature. Sodium perchlorate was prepared from sodium carbonate and perchloric acid and its concentration was determined as reported previously.[4] For some experiments sodium iodide was used in place of potassium iodide to minimize precipitation of potassium perchlorate.

Procedure. The aqueous solutions of I_2 and I_3^- interfere with the spectrophotometric determination of chlorine dioxide. Therefore,

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(1) F. Feldman and G. Gordon, *Inorg. Chem.*, **3**, 1728 (1964).
(2) G. Gordon and K. Kern, *ibid.*, **3**, 1055 (1964).
(3) D. M. H. Kern and G. Gordon, "Theory and Structure of Complex Compounds," Pergamon Press, New York, N. Y., 1964, pp 655–660.
(4) P. H. Tewari and G. Gordon, *J. Phys. Chem.*, 70, 200 (1966).
(5) R. C. Thompson and G. Gordon, *Inorg. Chem.*, **5**, 557 (1966).
(6) R. C. Thompson and G. Gordon, *ibid.*, **5**, 562 (1966).
(7) For example, in aqueous solutions when sodium chlorite and sodium hypochlorite are mixed, the reaction mechanism is consistent with an intermediate of the type $[Cl_2O_2]$ which can either disproportionate in concentrated solution to form chlorine dioxide and chlorine or in dilute solution to form chlorate and chloride. A similar intermediate is proposed in the disproportionation of chlorous acid and in the reaction between uranium(IV) and sodium chlorite.
(8) H. Taube and H. Dodgen, *J. Am. Chem. Soc.*, **71**, 3330 (1949).
(9) W. C. Bray, *Z. Physik. Chem.*, **54**, 575 (1906).

the iodine–triiodide isosbestic point at 4677 A was used to monitor the reaction. At this wavelength, the absorption due to chlorine dioxide is negligible. The reactants were mixed for each experiment with a spring-powered syringe,[10] and the course of the reaction was monitored spectrophotometrically by means of a Cary 14 spectrophotometer. No interaction between the stainless steel needle of the syringe and the reactant solutions could be detected spectrophotometrically. Quartz spectrophotometer cells (1-cm path length) were used as the reaction vessel.[4,6,10] The ionic strength and pH were adjusted with sodium perchlorate and sodium borate buffer, respectively. A Beckman Model GS pH meter was used to determine the hydrogen ion concentration. For the very rapid reactions, the output of the phototube preamplifier of the Cary spectrophotometer was followed directly by means of an oscilloscope which could be photographed with an attached Polaroid camera. The extinction coefficients and absorption spectra for the I_2–I_3^- system have been reported by several authors.[11–13] For these experiments, the molar extinction coefficients of I_2 and I_3^- were measured by the method reported by Awtery and Connick.[14] At ionic strength of 0.75 in the pH region of 4 to 8, the isosbestic point for the I_2–I_3^- system was found at 4677 ± 2 A in the temperature range 5–35°. Molar extinction coefficients of 650, 700, 738, and 710 M^{-1} cm^{-1} were found at 5, 15, 25, and 35°, respectively. For all measurements the Lambert-Beer law was obeyed, and the absorption due to potassium iodide, sodium perchlorate, sodium chlorite, and sodium borate was negligible.

Results and Discussion

The over-all reaction between aqueous solutions of chlorine dioxide and potassium iodide can be expressed by

$$2ClO_2 + 2I^- \longrightarrow 2ClO_2^- + I_2 \qquad (1)$$

When solutions of potassium iodide are injected into aqueous chlorine dioxide solutions, a rapid increase of the absorbance is observed followed by gradual decrease of the absorbance. In the presence of excess potassium iodide, the maximum absorbance occurs within about 0.1 sec. From the measured absorbance at long times, the final concentration of iodine and triiodide ion can be calculated. The maximum in the absorbance *vs.* time curve is assumed to correspond to an intermediate in the reaction. Thus, it is proposed that the initial reaction corresponds to the rapid formation of the intermediate followed by its relatively slow decomposition, as shown below.[15]

$$ClO_2 + I^- \xrightarrow{k_1} [ClO_2 \cdot I^-] \quad \text{(fast)} \qquad (2)$$

$$[ClO_2 \cdot I^-] \xrightarrow{k_2} ClO_2^- + I \quad \text{(slow)} \qquad (3)$$

$$I + I \longrightarrow I_2 \quad \text{(very fast)} \qquad (4)$$

The rate law for these reactions corresponds to

$$-d[ClO_2]/dt = k_1[ClO_2][I^-] \qquad (5)$$

$$-d[ClO_2 \cdot I^-]/dt = k_2[ClO_2 \cdot I^-] - k_1[ClO_2][I^-] \qquad (6)$$

Under pseudo-first-order conditions, when the initial iodide ion concentration, $[I^-]_0$, is much larger than the initial concentration of chlorine dioxide, $[ClO_2]_0$, the integrated expression is

$$[ClO_2 \cdot I^-] = [ClO_2]_0 \frac{k'_1}{k'_1 - k_2}(e^{-k_2t} - e^{-k'_1t}) \qquad (7)$$

$$[\Sigma I_2] = 0.5[ClO_2]_0 + 0.5[ClO_2]_0\left[\frac{k_2}{k'_1 - k_2}e^{-k'_1t} - \frac{k'_1}{k'_1 - k_2}e^{-k_2t}\right] \qquad (8)$$

where k'_1 is the pseudo-first-order constant, k_1 times the iodide ion concentration, and $[\Sigma I_2] = [I_2] + [I_3^-]$.

Under the conditions of the reaction $k'_1 >> k_2$ and $k'_1/(k'_1 - k_2) \approx 1$ and $k_2/(k'_1 - k_2)e^{-k'_1t} \approx 0$; this allows for simplification of eq 7 and 8 to

$$[ClO_2 \cdot I^-] = [ClO_2]_0[e^{-k_2t} - e^{-k'_1t}] \qquad (9)$$

$$[\Sigma I_2] = 0.5[ClO_2]_0[1 - e^{-k_2t}] \qquad (10)$$

The absorbance A of the reactants and products in the 1-cm cell is given by

$$A = \epsilon_1[ClO_2 \cdot I^-] + \epsilon_2[\Sigma I_2] = [ClO_2]_0e^{-k_2t}(\epsilon_1 - 0.5\epsilon_2) - [ClO_2]_0\epsilon_1e^{-k'_1t} + 0.5\epsilon_2[ClO_2]_0 \qquad (11)$$

where ϵ_1 and ϵ_2 are the molar extinction coefficients of the intermediate and the $[I_2 + I_3^-]$ system at the isosbestic point. If eq 9 and 10 are substituted in eq 11, and this is followed by differentiation with respect to time, the time of maximum absorbance, δ, is obtained from $dA/dt = 0$. Thus

$$\delta = \frac{\ln\left(\frac{k'_1}{k_2}\right)\frac{\epsilon_1}{\epsilon_1 - 0.5\epsilon_2}}{k'_1 - k_2} \qquad (12)$$

The molar extinction coefficient ϵ_1 of the intermediate is derived directly from eq 11

$$\epsilon_1 = \frac{A - \epsilon_2(\Sigma I_2)}{[ClO_2 \cdot I^-]} \qquad (13)$$

The concentrations $[ClO_2I^-]$ and $[\Sigma I_2]$ are determined by eq 9 and 10. A nonlinear least-squares fit of the absorbance *vs.* time data can be calculated directly[16] from eq 11. The best fit for a typical set of data shown in Table I was obtained with $k'_1 = 70 \pm 7$ sec^{-1}, $k_2 = 0.10 \pm 0.01$ sec^{-1}, and $\epsilon_1 = 565 \pm 18$ M^{-1} cm^{-1}. The time of maximum absorbance, δ, corresponded to 0.109 sec and was independent of initial chlorine dioxide

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(10) R. C. Thompson and G. Gordon, *J. Sci. Instr.*, 41, 480 (1964).

(11) J. J. Caster and S. Notelson, *Anal. Chem.*, 21, 1005 (1949).

(12) L. I. Katzin and E. Gebert, *J. Am. Chem. Soc.*, 76, 2049 (1954).

(13) Y.-T. Chia, U. S. Atomic Energy Commission, UCRL-8311, June 1958.

(14) A. D. Awtery and R. E. Connick, *J. Am. Chem. Soc.*, 73, 1842 (1951).

(15) The formation of I· from I^- and ClO_2 followed by the fast formation of I_2^- from I· and I^- is also consistant with observed formation of the intermediate. The disappearance of an I_2^- intermediate would be expected to be second order in contrast to the first-order disappearance observed for the $[ClO_2 \cdot I^-]$ intermediate.

(16) The computer time for this project was supported in part through the facilities of the Computer Science Center Laboratory of the University of Maryland. A detailed description of the program appears in Los Alamos publication LA-2367.

concentration as would be expected from eq 12. The results for a series of experiments as a function of initial chlorine dioxide concentration are shown in Table II.

Table I. Typical Pseudo-First-Order Rate Data[a] for the Chlorine Dioxide–Potassium Iodide Reaction at 25°

Time, sec	Absorbance	$[ClO_2I^-]$, $M \times 10^4$	$[\Sigma I_2]$, $M \times 10^4$
0.05	0.254	4.62	~0
0.1	0.270	4.72	0.0212
1	0.260	4.31	0.227
2	0.251	3.91	0.431
3	0.244	3.53	0.610
4	0.237	3.19	0.786
5	0.232	2.89	0.938
10	0.206	1.76	1.51
15	0.195	1.06	1.85
20	0.188	0.64	2.03
30	0.182	0.24	2.26
40	0.178	0.087	2.34
50	0.176	0.032	2.37

[a] $[ClO_2]_0 = 4.77 \times 10^{-4}\ M$, $[I^-]_0 = 2.45 \times 10^{-2}\ M$, $\mu = 0.75\ M$, pH 8.5, measured at 4677 A.

Table II. Rate Constants for the Chlorine Dioxide–Potassium Iodide Reaction[a] at 25°

$[ClO_2]_0$, $M \times 10^4$	$[I^-]_0$, $M \times 10^2$	k'_1, sec^{-1}	k_2, sec^{-1}	ϵ_1, $M^{-1}\ cm^{-1}$	δ_{calcd}, sec
1.19	2.31	69 ± 7[b]	$0.10_1 \pm 0.01$[b]	550 ± 20	0.11_1
1.41	2.45	70 ± 5	$0.09_8 \pm 0.01$	565 ± 12	0.10_9
2.26	2.45	72 ± 8	0.10 ± 0.01	575 ± 22	0.10_6
4.77	2.45	70 ± 7	0.10 ± 0.01	568 ± 18	0.10_9
5.26	2.45	71 ± 6	0.10 ± 0.01	565 ± 16	0.10_8
Average		70 ± 7	0.10 ± 0.02	565 ± 18	0.10_8

[a] At pH 8.5. [b] The deviations correspond to deviations from the mean for replicate experiments.

The results shown in Tables I and II are used as evidence that the reaction is first order with respect to chlorine dioxide in the formation of the intermediate and first order with respect to $[ClO_2I^-]$ for decomposition of the intermediate.

An additional series of experiments was carried out as a function of pH in the range 5.0–8.5. The effect of pH was negligible in that rate constants within the experimental error of those found at pH 8.5 were observed. It is concluded that the reaction is independent of pH. Some difficulties were encountered, however, owing to the reaction between I^- and the product ClO_2^- at pH values below 6. This resulted in the production of more I_2–I_3^- species, as shown below and reported elsewhere.[17,18] The effects were small but

$$ClO_2^- + 4H^+ + 4I^- = 2I_2 + 2H_2O + Cl^- \qquad (14)$$

limited the pH to a minimum of 5.0, since reaction 14 is hydrogen ion dependent.[18]

Another series of experiments was carried out at pH 8.5 to determine the effect of the product ClO_2^- on the rate of the reaction. With $4.8 \times 10^{-4}\ M$ ClO_2 and $3.6 \times 10^{-2}\ M > [ClO_2^-] > 3.5 \times 10^{-3}\ M$, no effect on the rate of the reaction was observed at pH 8.5 at 25°.

Experiments as a function of temperature are listed in Table III. The results at each temperature are the average of at least three experiments.

Table III. Rate Constants as a Function of Temperature ($4.8 \times 10^{-4}\ M$ ClO_2 and $2.45 \times 10^{-2}\ M$ KI)

Temp, °C	k'_1, sec^{-1}	k_2, sec^{-1}	δ, sec	ϵ_1, $M^{-1} cm^{-1}$
5	$28._5 \pm 4$	$0.08_5 \pm 0.02$	0.245	477 ± 22
15	45 ± 5	$0.09_0 \pm 0.02$	0.160	568 ± 19
25	70 ± 8	$0.10_0 \pm 0.02$	0.108	565 ± 18
35	110 ± 10	$0.10_7 \pm 0.04$	0.073	535 ± 24

The effect of iodide ion on the rate of formation of $[ClO_2I^-]$ was determined by variation of the initial iodide ion concentration. The equation

$$\frac{1}{[I^-]_0 - [ClO_2]_0} \ln \frac{[ClO_2]_0[I^-]}{[I^-]_0[ClO_2]} = k_1 t \qquad (15)$$

is consistent with reaction 2 and eq 5. Since the absorption due to $[\Sigma I_2]$ is negligibly small in the early stages of the intermediate formation (< 0.1 sec), and, since k_1 is much larger than k_2, it can be seen that $A \approx \epsilon_1 [ClO_2I^-]$. Accordingly, the concentrations of chlorine dioxide and iodide ion can be written as

$$[ClO_2] = [ClO_2]_0 - (A/\epsilon_1) \qquad (16)$$

$$[I^-] = [I^-]_0 - (A/\epsilon_1) \qquad (17)$$

By introducing the results of eq 16 and 17 into eq 15, the second-order rate constant can be determined by standard techniques. A graph of the left side of eq 15 against time at 25° is shown in Figure 1. It was found that the plots were linear, corresponding to a reaction first order with respect to chlorine dioxide and first order with respect to iodide ion. The results of the second-order rate constant as a function of temperature are listed in Table IV.

Table IV. Second-Order Rate Constants for the Formation of $[ClO_2I]^-$ as a Function of Temperature

Temp, °C	5	15	25	35
$10^3 k_1$, $M^{-1} sec^{-1}$	1.12	1.83	2.95	4.64

The activation enthalpy and entropy for the process shown in eq 2 (*i.e.*, the formation of the intermediate) in sodium borate buffer at $\mu = 0.75\ M$ and pH 8.5 was calculated from the temperature-dependence data

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(17) A. Indelli, *J. Phys. Chem.*, **68**, 3027 (1964).

(18) D. M. H. Kern and C.-H. Kim, *J. Am. Chem. Soc.*, **87**, 5309 (1965).

by means of a nonlinear least-squares computer program.[16] Eyring's absolute reaction rate theory

$$k = (k_b/h)T \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) \quad (18)$$

was used in the calculation.[19] The resulting values are shown in Table V. The activation enthalpy for the reaction between ClO_2 and I^- is somewhat lower than the value reported[17,18] for the reaction between ClO_2^- and I^-. The activation parameters for the equation corresponding to the disappearance of the intermediate have considerably larger uncertainties due to the uncertainty associated with the reported rate constant, k_2.

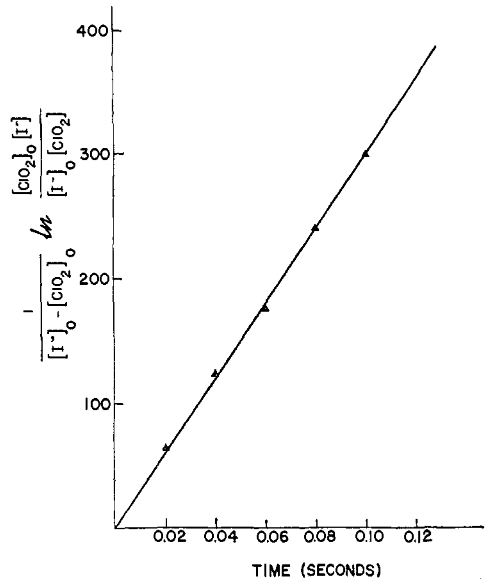

Figure 1. Second-order plot for the ClO_2-KI reaction in aqueous solution.

The value of ΔH^* for eq 3 is 0.8 ± 0.2 kcal/mole. The entropy of activation is not reported in that the resulting value of ΔS^* is quite a negative value, which suggests a very negative entropy for the transition state which is inconsistent with the observation of entropies of nearly zero for unimolecular decompositions. This appears to be a manifestation of the small changes and large uncertainties in k_2 observed as a function of temperature.

Table V. Activation Parameters for the ClO_2-I^- Reaction

	ΔH^*, kcal/mole	ΔS^*, eu
k_1 (eq 2)	7.4 ± 0.2	−17 ± 3
ClO_2^--I^- reaction[17,18]	12.3	+21

Possible side reactions which might interfere with an exact determination of the rate constants k_1 and k_2 include the subsequent reaction between ClO_2^- and I^- and the disproportionation of ClO_2 with base. The ClO_2^--I^- reaction in aqueous solution is catalyzed by the iodine product, but the autocatalysis is inhibited by iodide ion. Kern and Kim[18] and Indelli[17] have shown the rate law for eq 14 to be

$$d[\Sigma I_2]/dt = 920[ClO_2^-][I^-]A_{H^+} + 0.005[ClO_2^-][I_2]/[I^-] \quad (19)$$

at 25° and an ionic strength of 0.5 M over the pH range 4–8. Thus for our experiments at pH 8.5 this reaction is of no concern, and at pH 5.5 it makes at most a minor contribution near the end of the reaction.

The base disproportionation of chlorine dioxide

$$2ClO_2 + 2OH^- \rightleftharpoons ClO_2^- + ClO_3^- + H_2O$$

is slow enough at pH 8.5 so that it also does not complicate the observed reactions.[9,20] Additional evidence for this point is that the final concentrations of ($I_2 + I_3^-$) corresponded precisely to the amount predicted on the basis of eq 2 and 3.

Several experiments were also carried out in an attempt to map out the spectrum of the $[ClO_2I^-]$ intermediate in the vicinity of the I_2-I_3^- isosbestic point. Owing to the complication[11-14] of the I_2-I_3^- equilibrium away from the isosbestic point, only two wavelengths, 4400 and 4800 A, were chosen, and the experiments were carried out at 25°. A summary of the observed extinction coefficients is shown in Table VI.

Table VI. Extinction Coefficients at 25°

Wavelength, A	ϵ_1, $[ClO_2I^-]$, M^{-1} cm^{-1}	ϵ_2, $[I_2 + I_3^-]$, M^{-1} cm^{-1}
4400	1770	926
4677	565	738
4800	470	349

Although there is no direct evidence for the structure of the $[ClO_2I^-]$ intermediate, the nucleophilic character[21,22] of the ClO_2 and ClO_2^- and the results of Thompson and Gordon[5,6] on the oxidation of chromium(II) by ClO_2 and ClO_2^- would seem to suggest the structure i with a direct chlorine–iodine bond. How-

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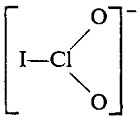
(19) S. Glasstone, K. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p 199.

(20) W. Buser and H. Hanisch, *Helv. Chim. Acta*, **35**, 2547 (1952).

(21) R. W. Johnson and J. O. Edwards, *Inorg. Chem.*, **5**, 2073 (1966).

(22) J. O. Edwards, *J. Am. Chem. Soc.*, **76**, 1540 (1954).



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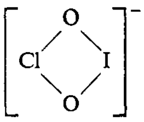

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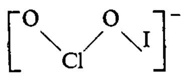

iii

ever, this does not preclude other possibilities such as ii or iii.

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