TABLE IV

THE ANGLES BETWEEN THE Hg–Cl BONDS OF
NEIGHBORING MOLECULES

		Hg–Cl₁	Hg–Cl₂
Hg–Cl₁	Zeeman anal	$77° 0' \pm 5'$	
	X-ray anal[5]	$75° 33'$	
	X-ray anal[6]	$86° 20'$	
Hg–Cl₂	Zeeman anal	$77° 0' \pm 4'$	$77° 0' \pm 1'$
	X-ray anal[5]	$77° 45'$	$79° 59'$
	X-ray anal[6]	$86° 5'$	$85° 51'$

TABLE V

THE ANGLES BETWEEN THE CRYSTAL AXES (a, b, c) AND THE
PRINCIPAL AXES OF THE FIELD GRADIENTS (x, y, z) IN
HgCl₂ CRYSTAL

		a axis	b axis	c axis
x axis		$26'$	$90° 11'$	$90° 34'$
y axis		$90° 10'$	$51° 32'$	$141° 31'$
z axis	Zeeman anal	$90° 4'$	$38° 30'$	$51° 30'$
	X-ray anal[5]	$90° 0'$	$38° 50'$	$51° 7'$
	X-ray anal[6]	$90° 0'$	$43° 2'$	$46° 58'$

of the Hg–Cl bond can be determined from the observed values of the quadrupole coupling constant and the asymmetry parameter by the following equations,[9] because the molecule HgCl₂ is thought to be linear as stated above.

The number of unbalanced p electrons U_p is evaluated from the observed quadrupole coupling constant $(eQq_{zz})_{obsd}$ by the equation

$$U_p = (eQq_{zz})_{obsd}/(eQq_{zz})_{atom} \qquad (7)$$

where $(eQq_{zz})_{atom}$ is the quadrupole coupling constant in a free chlorine atom, 109.7 Mc/sec.[10]

On the other hand, the value U_p is related to the

(9) S. Kojima, K. Tsukada, and Y. Hinaga, *J. Phys. Soc. Japan*, **10**, 493 (1955).

(10) V. Jaccarino and L. G. King, *Phys. Rev.*, **83**, 471 (1951).

ionic character i and the double bond character f as in the equation

$$U_p = (1 - i - f)(1 - s) + (1 + \epsilon)(1 - 2s)/2 \quad (8)$$

where s is the s electron character and is equal to 0.15 and ϵ is the shielding effect due to an outer electron and is equal to 0.15.[11,12]

The asymmetry parameter η is expressed by the values of U_p and f as follows[9,13]

$$\eta = (q_{xx} - q_{yy})/q_{zz} = (3/2)f(1 + \epsilon)/U_p \qquad (9)$$

From eq 7, 8, and 9, U_p, i, and f are determined as shown in Table VI. It is found that the present value of the ionic character is nearly equal to 54%, which was obtained theoretically by Pearson and Gray.[14]

TABLE VI

THE BOND NATURE OF Hg–Cl IN MERCURIC CHLORIDE

	U_p, %	i, %	f, %
Hg–Cl bond for ν_1	40.5	52.5	2.1
Hg–Cl bond for ν_2	40.2	52.6	2.0

In the light of the X-ray analysis, the bond lengths of the two kinds of Hg–Cl are 2.23 and 2.27 A, and the environments of the chlorine atoms are not similar. From the present results, however, it is concluded that there is no so significant difference in bond nature between the two bonds.

(11) C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949).

(12) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p 237.

(13) U. Gordy, W. V. Smith, and R. F. Trambalulo, "Microwave Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1953, p 286.

(14) R. G. Pearson and H. B. Gray, *Inorg. Chem.*, **2**, 358 (1963).

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Kinetics of the Permanganate Ion–Chloride Ion Reaction[1a]

BY K. J. LIU, H. LESTER,[1b] AND N. C. PETERSON

The rate of the reaction between permanganate ion and chloride ion in perchloric acid–sodium perchlorate solutions was measured by a spectrophotometric method. The reaction was found to be first order in permanganate ion, second order in chloride ion, and third order in hydrogen ion. The rate law was given by $-d(MnO_4^-)/dt = k(MnO_4^-)(Cl^-)^2(H^+)^3$, and the composition of the transition state required by this rate law is $H_3MnO_4Cl_2$. This reaction is much faster than the reaction of Mn(III) with chloride so that the over-all reaction for this rate law is $MnO_4^- + 4Cl^- + 8H^+ = Mn^{3+} + 2Cl_2 + 4H_2O$. The influence of sodium perchlorate concentration on reaction rate was measured, and the rate was found to increase with increasing salt concentration above 0.75 M. The sixth-order rate constant was $(5.20 \pm 0.58) \times 10^{-2} M^{-5} sec^{-1}$ at 27.9° and 3.0 M ionic strength. The activation energy was 17.7 ± 2.3 kcal mole^{-1}.

Introduction

No prior kinetic data for the permanganate–chloride reaction have been published although the chloride

interference with the end point of the permanganate titration of iron(II) has been known for a long time.[2]

Ibers and Davidson[3] have shown that permanganate reacts with chloride ion in hydrochloric acid solu-

(1) (a) Part of this work was abstracted from the M.S. thesis of K. J. Liu, Ladd Chemical Laboratory, North Dakota Agricultural College, Fargo, N. D., 1959; (b) National Science Foundation, Summer Research Fellow, summer 1961.

(2) C. Zimmerman, *Ann.*, **213**, 285 (1882).

(3) J. A. Ibers and N. Davidson, *J. Am. Chem. Soc.*, **72**, 4744 (1950).

tions to produce manganese(III). The manganese-(III) can further oxidize chloride to produce Mn^{2+} and chlorine; however, Ibers and Davidson found that, although the equilibrium was favorable, the reaction was extremely slow in the absence of a catalyst such as silver(I), copper(II), platinum(IV), and lead(II), and manganese(III) persists for days or weeks.

Permanganate ion is intensely colored and follows Beer's law permitting the rate of disappearance of permanganate to be followed by means of a spectrophotometer. At the absorption maximum of permanganate ion of 525 mμ the reaction products (manganese-(III)) have an absorptivity only 2.7% of that for permanganate ion.

Experimental Section

Reagents.—Stock solutions of perchloric acid and hydrochloric acid were prepared from ACS reagent grade chemicals and standardized against sodium hydroxide solution previously standardized against potassium acid phthalate. Sodium perchlorate stock solution was prepared by neutralizing sodium hydroxide with perchloric acid and computing the concentration from the measured volumes and initial concentrations.

Stock solutions of potassium permanganate were prepared from the analytical reagent and distilled water and were stored in the dark.

Stoichiometry.—Potassium permanganate was allowed to react with excess 5 M hydrochloric acid in a separatory funnel, the chlorine was extracted into carbon tetrachloride, and the absorbance of the carbon tetrachloride layer was measured at 327 mμ using 1-cm cells and a Cary Model 14 spectrophotometer. The procedure of Sherman and Strickland[4] was followed in detail. An average of 2.02s mole of chlorine/mole of permanganate was obtained for eight determinations, requiring the stoichiometric reaction to be

$$MnO_4^- + 8H^+ + 4Cl^- = Mn^{3+} + 2Cl_2 + 4H_2O$$
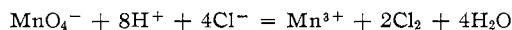
Measurement of Reaction Rates.—The reaction rates were determined spectrophotometrically by following the permanganate absorption at various times. A Bausch and Lomb Model Spectronic 20 colorimeter equipped with a thermostated Roto Cell (Arthur H. Thomas Co.) was used. The absorbance was measured at the absorption maximum of permanganate at 525 mμ. The absorbance due to products, A_p, was measured at a time longer than 10 half-lives. The first-order rate constants were insensitive to the exact value of A_p. The steady-state temperature of the reaction mixture in the spectrophotometer was slightly higher than the bath temperature and was measured using a Western Electric 14A thermistor in a Wheatstone bridge circuit. The thermistor was calibrated against a National Bureau of Standards certified thermometer. A solution containing sodium perchlorate, perchloric acid, and hydrochloric acid was equilibrated in a constant-temperature bath, together with a solution of potassium permanganate. The solutions were mixed and a sample was placed in the absorption cell. The flasks were wrapped with aluminum foil to avoid photochemical effects. In experiments to determine the kinetic order, concentrations were adjusted to give an ionic strength of 3.00 M, with hydrogen ion concentrations 1.5–3.0 M. Another series of rate measurements was made having various values of the total ionic strength from 0.5 to 3.5 M.

Order of Reaction.—Permanganate ion was found to obey Beer's law at the absorption maximum of 525 mμ. The reaction products were found to have a small absorption (about 2.7% of the initial permanganate absorbance at 525 mλ in the absence of added Mn^{2+}). The absorbance of solutions of Mn^{2+} at 525

(4) M. I. Sherman and J. D. H. Strickland, *Anal. Chem.*, **27**, 1778 (1955).
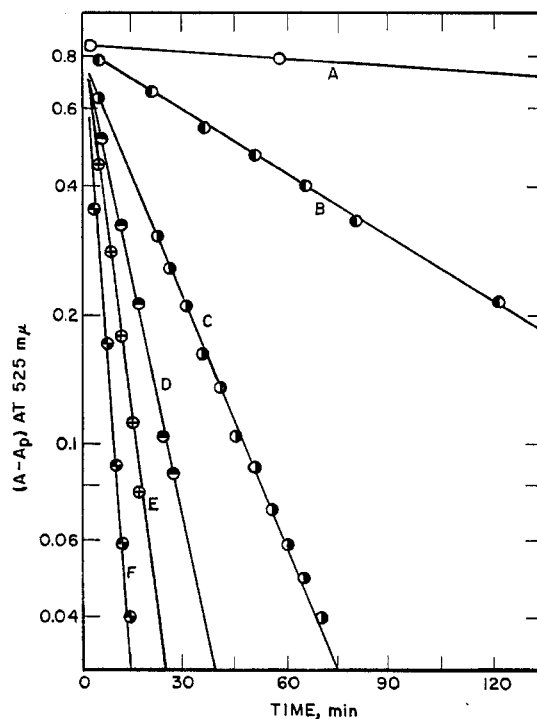

Figure 1. Pseudo-first-order (semilog) plots of the permanganate reaction. Ionic strength 3.00 M; hydrogen ion concentration 3.00 M. Chloride ion concentration: A, 0.000; B, 0.00104; C, 0.0208; D, 0.0312; E, 0.0416; F, 0.0520 M. Temperature 27.9°.

mμ for these concentrations is too small to measure. The manganese(III) formed was found to react at a rate which was about two orders of magnitude slower, so that in the times characteristic of our experiments the stoichiometry of the reaction is

$$MnO_4^- + 4Cl^- + 8H^+ \longrightarrow Mn^{3+} + 2Cl_2 + 4H_2O$$
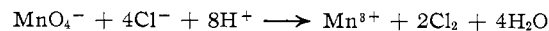
where the identity of the manganese(III) species is unknown.

The reaction rate was found to be represented by an over-all rate law of the form

$$-d(MnO_4^-)/dt = k(MnO_4^-)^p(Cl^-)^q(H^+)^r \qquad (1)$$

The initial concentrations of chloride ion and hydrogen ion are in large excess over the stoichiometric amounts, so that the rate equation (1) can be integrated taking $k(Cl^-)^q(H^+)^r$ as constant. The reaction appears to be pth order in such an experiment (pseudo-pth order). Pseudo-first-order plots of log $(A - A_p)$ *vs.* time gave good straight lines to 90% completion. Examples are in Figure 1, where A is the absorbance at time t and A_p is the absorbance of the products, measured at a time much longer than the half-life for each kinetic run; thus the reaction is first order in permanganate.

The chloride ion concentration was varied over the range which gave convenient rates at constant hydrogen ion concentration. Plots of log k_1 *vs.* log (Cl^-) were linear, at constant (H^+), with an average slope of 1.94, indicating the reaction is second order in chloride ion. These are shown in Figure 2.

Similarly log k_1 *vs.* log (H^+) was plotted using values obtained from the above graphs at six values of (Cl^-). The plots were linear and the slopes were 3.19–3.30 with an average value 3.21, indicating the reaction is third order in hydrogen ion. Permanganate slowly decomposes in perchloric acid solutions in absence of chloride ion, probably by oxidation of water, but this side reaction was found to have a negligible rate compared to the reaction with chloride ion. Results are summarized in Tables I and II. The sixth-order rate constant was calculated from

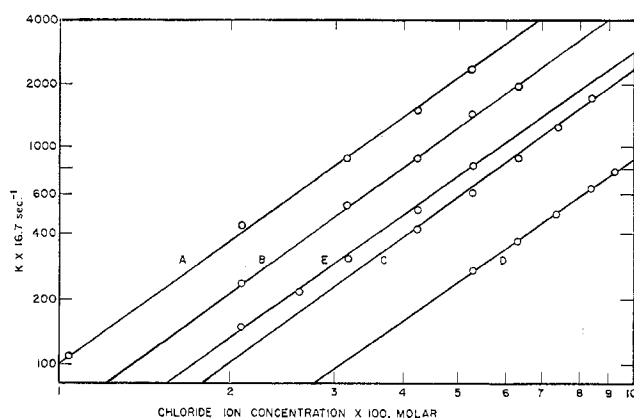$$k_6 = \frac{k_1}{(H^+)^3(Cl^-)^2} \qquad (2)$$

Figure 2. Plots for determining order in chloride ion. Hydrogen ion concentration: A, 3.00; B, 2.50; C, 2.00; D, 1.50; E, 3.00 M. Temperature is 27.9°, except for D where it is 18.3°.

TABLE I

OBSERVED RATE CONSTANTS FOR THE PERMANGANATE–CHLORIDE REACTION AT 27.9° [a]

(H^+), M	(Cl^-), M	$10^4 k_1$, sec^{-1}	$10^2 k_6$, M^{-5} sec^{-1}
3.00	0.0000	0.00963	...
	0.0104	1.84	6.28
	0.0208	7.55	6.47
	0.0312	14.90	5.67
	0.0416	24.00	5.13
	0.0520	38.30	5.25
2.50	0.0208	3.85	5.70
	0.0312	9.03	5.93
	0.0416	14.62	5.40
	0.0520	23.87	5.65
	0.0624	31.11	5.12
2.00	0.0416	6.98	5.05
	0.0520	10.18	4.72
	0.0624	13.86	4.45
	0.0728	20.20	4.82
	0.0832	28.08	5.07
1.50	0.0520	4.47	4.83
	0.0624	6.13	4.67
	0.0728	8.17	4.57
	0.0832	10.10	4.33
	0.0936	12.90	5.02

Mean 5.20 ± 0.58

[a] The reaction in the absence of chloride was followed to 40% completion and was first order. This reaction is probably the oxidation of water. The indicated uncertainty is the standard deviation. $(MnO_4^-)_0 = 0.000401\ M$; $\mu = 3.00$.

TABLE II

RATE CONSTANTS FOR THE DISAPPEARANCE OF PERMANGANATE ION AT 18.3° [a]

(Cl^-), M	$10^4 k_1$, sec^{-1}	$10^2 k_6$, M^{-5} sec^{-1}
0.0104	0.61	2.08
0.0208	2.36	2.03
0.0260	3.47	1.92
0.0312	5.12	1.95
0.0416	8.05	1.72
0.0520	13.73	1.83

Mean 1.93 ± 0.13

[a] $\mu = (H^+) = 3.00\ M$; $(MnO_4^-)_0 = 0.000401\ M$.

The addition of manganous sulfate is reported to diminish the chloride error in the titration of iron with permanganate.[2] The rate of disappearance of permanganate ion was measured in solutions containing manganous sulfate with and without chloride

TABLE III

RATE OF DISAPPEARANCE OF PERMANGANATE ION IN SOLUTIONS CONTAINING MANGANOUS SULFATE AT 27.9° [a]

$(MnSO_4)$, M	(Cl^-), M	$10^4 k_1$, sec^{-1}
0.00963	0.0104	16.5
0.00963	0.0000	14.0
0.00000	0.0104	1.83
0.00100	0.0312	16.3
0.00200	0.0312	18.4
0.00400	0.0312	21.9
0.00600	0.0312	28.4
0.0144	0.0312	70.8
0.0193	0.0312	115.1

[a] $(H^+) = \mu = 3.0\ M$; $(MnO_4^-)_0 = 0.000401\ M$.

ion. Pseudo-first-order kinetics were observed in these experiments also, and the results are summarized in Table III.

It was found that added manganous sulfate increases the rate of disappearance of permanganate. No MnO_2 was observed to precipitate from the reaction mixtures, but the absorption of products increased with increasing Mn^{2+} concentration, evidence for the stoichiometric reaction: $MnO_4^- + 4Mn^{2+} + 8H^+ = 5Mn^{3+} + 4H_2O$.

Comparing the rates in the first three experiments listed in Table III, it is evident that within experimental error the rate constant in the presence of Mn^{2+} and Cl^- together is the sum of the rate constants in blank experiments in which the Mn^{2+} and Cl^- were added individually at the same concentration as in the first experiment.

A plot of log $(k - k_{Cl^-})$ vs. log (Mn^{2+}) was found to give a straight line of slope 2, suggesting a reaction second order in manganous ion where k_{Cl^-} is the first-order rate constant estimated for the permanganate–chloride reaction. Recently, Rosseinsky and Nicol[5] have measured the rate of the permanganate–manganous reaction in perchlorate media and reported kinetics first order in permanganate and second order in manganese(II).

Tentatively it is suggested that permanganate is reduced by two parallel reaction paths in mixtures containing both chloride and manganous ions. It is planned to investigate the effect of anions on the rate of the manganous–permanganate reaction in further work.

The sixth-order rate constants in Tables I and II tend to increase slightly with increasing (H^+), consistent with an order slightly higher than 3.0. The maximum variation in k_6 was 33% as the hydrogen ion concentration was changed from 1.5 to 3.0 M at 27.9°. This variation is probably due to medium effects.

An estimate of the Arrhenius activation energy was calculated from the averages of k_6 at 27.9 and 18.3° and was 17.7 ± 2.3 kcal mole^{-1}.

Discussion

These data are consistent with Edwards' type-four mechanism for reactions of oxy anions with bases.[6] Edwards cites only two other examples of this mechanism with a third-order dependence on hydrogen ion.

A mechanism of this type consistent with the sixth-order rate law may be written which has the required transition state composition $H_3MnO_4Cl_2$. The number of water molecules in the transition state is unknown because of the usual kinetic ambiguities.

Clearly, several bimolecular reaction steps are required to produce this transition state from H^+, MnO_4^-, and Cl^-. We speculate that a likely mechanism involves formation of a small equilibrium concen-

(5) D. R. Rosseinsky and M. J. Nicol, *Trans. Faraday Soc.*, **61**, 2718 (1965).

(6) J. O. Edwards, *Chem. Rev.*, **50**, 455 (1952).