Summary

Five filters commonly used to isolate λ 3130 Å. from the mercury arc spectrum have been critically evaluated over a range of concentrations. Cobaltous chloride was found to be of doubtful value. The combination of a 50-mm. length of 0.178 *M* nickel chloride, 50 mm. of 0.0005 *M* potassium chromate, 10 mm. of 0.0245 *M* potassium biphthalate, and 5 mm. of Red Purple Corex glass (Corning No. 9863), reduces extraneous ultraviolet radiation to less than 0.01%. About 25% of the 3130 Å group is transmitted. With a high-pressure arc, in which the desired triplet is broadened, the above filters restrict the radiation to the region 3100–3300 Å.

ROCHESTER, N. Y. RECEIVED JANUARY 16, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO]

Catalysis of the Reaction of Chlorine and Oxalic Acid. Complexes of Trivalent Manganese in Solutions Containing Oxalic Acid

BY HENRY TAUBE

In the present study observations on the catalysis by manganic ion of the reaction

$$H_2C_2O_4 + Cl_2 = 2H^+ + 2Cl^- + 2CO_2$$

are reported. Analysis of the rate data accumulated in the study of this case of homogeneous catalysis has led to conclusions about the stability of complexes of trivalent manganese and oxalate in solutions containing hydrochloric acid and about the mechanism of the relatively slow net disappearance of the catalyst in the system.

Important conclusions can be drawn from qualitative observations which may be made on the system under study. If Mn(III), in solution as the sulfate complex, for example, is added to a solution 2 *M* in hydrochloric acid and containing also oxalic acid, the color of the trivalent manganese is discharged almost instantly. If, however, the acid solution contains also both chlorine and manganous ion, the color of trivalent manganese[1] persists for long periods of time—it has been observed up to twenty minutes—although it does eventually disappear. It is observed that chlorine does not oxidize manganous ion to the manganic state at an appreciable rate under the prevailing conditions. The persistence of manganic ion when manganous ion and chlorine are present simultaneously can therefore not be a simple equilibrium phenomenon. The direct experiment of comparing the color of a solution made up as above with one from which oxalic acid is absent, establishes that manganic ion is associated with oxalate even at 2 *M* hydrochloric acid.

Quantitative investigation of the system shows that during the time in which Mn(III) exists in the solutions described, the reaction of chlorine and oxalic acid proceeds at a greatly enhanced rate, and that manganous ion alone exerts no noticeable effect on the rate of this reaction. The rate of reaction of chlorine and oxalic acid has been measured as a function of the concentration variables, time and the temperature.

The data on the rate of reaction at zero time—when the catalyst has undergone no net decrease in concentration—are consistent with the following mechanism, and will be discussed with reference to it.[2]

Mn(III) in the solutions under investigation, usually 2 *M* in hydrochloric acid, is distributed among the ions Mn_{Cl}^{+++}, $MnC_2O_4^+$ and $Mn(C_2O_4)_2^-$.[3] Equilibrium between these species is established rapidly, and the equilibria are formulated as

$$H_2C_2O_4 + Mn_{Cl}^{+++} \overset{K_a}{\rightleftharpoons} MnC_2O_4^+ + 2H^+ \quad (a)$$

$$H_2C_2O_4 + MnC_2O_4^+ \overset{K_b}{\rightleftharpoons} Mn(C_2O_4)_2^- + 2H^+ \quad (b)$$

The slow step in the series of reactions leading to catalysis of the reaction of chlorine and oxalic acid is the first order decomposition[2] of the ion $MnC_2O_4^+$

$$MnC_2O_4^+ \xrightarrow{k_1} Mn^{++} + C_2O_4^- \quad (1)$$

The following reactions are

$$C_2O_4^- + Cl_2 \xrightarrow{k_3} Cl + Cl^- + 2CO_2 \quad (3)$$

$$Cl + Mn^{+++} \xrightarrow{k_6} Mn^{+++} + Cl^- \quad (6)$$

Steps (3) and (6) together with the equilibria (a) and (b) account for regeneration of the catalyst.

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[1] Launer, THIS JOURNAL, **55**, 865 (1933), has shown that the net rate of decomposition of $Mn(C_2O_4)_3$ is decreased by oxygen, and that reduction of oxygen is induced by the decomposition of the complex ion.

[2] The form of the rate law agrees equally well with the slow step: $Mn^{+++} + C_2O_4^{=} \xrightarrow{k_1'} Mn^{++} + CO_2 + CO_2^-$. (1′) advanced by Launer.[5] A decision in favor of step 1 is made below (see Discussion) by arguments based on the variation of rate with temperature. No data published at present distinguish between $C_2O_4^-$ and CO_2^- as the reducing intermediate, nor, in fact, can Mn^+ be excluded as a possibility (see Discussion). The choice of $C_2O_4^-$ adopted here is quite arbitrary, and the specific rate established for the reducing intermediate may actually apply to CO_2^- or Mn^+.

[3] It is recognized that these ions associate with water, and the first at least, probably also with chloride ion. The formulas adopted are intended to imply a conclusion only about the ratio Mn(III) to $C_2O_4^{=}$ in the complex, and not to imply the absence of other interactions.

Steps (3) and (6) have been presented as reasonable possibilities in work already published,[4] and the consumption of atomic chlorine by reaction with Mn^{++} rather than by other paths is shown below to be consistent with other data.

Evidence from the present work for the existence in the solutions of the mono-oxalate as well as the dioxalate ions is the observed variation of the rate of reaction with the concentration of oxalic acid; this variation is accounted for quantitatively if the three ions above are assumed to be in equilibrium, but not if Mn_{Cl}^{+++} and $Mn(C_2O_4)_2^-$ are assumed as the only species. Visual comparisons of the color of solutions containing Mn(III), as the concentration of oxalic acid only changes, provide further evidence. Experiments by Launer[5] set an upper limit on the stability (to association–dissociation reaction) of the mono-oxalate complex; the conclusions about the stability of this complex reached in the present work are not in conflict with his observations. The existence of 1:1 complexes over intermediate ranges of concentration for the complexing ion has been demonstrated by a number of investigators.[6] The condition of low oxalate ion achieved in the present experiments by adding strong acid is favorable for realizing appreciable concentrations of the mono-oxalate complex.

The net decomposition of the catalyst as time progresses is accounted for by the steps (7) and (8)

$$C_2O_4^- + MnC_2O_4^+ \longrightarrow Mn^{++} + 2CO_2 + C_2O_4^= \quad (7)$$

$$C_2O_4^- + Mn_{Cl}^{+++} \longrightarrow Mn^{++} + 2CO_2 \quad (8)$$

The present work offers direct kinetic evidence for the above reactions. They are two of several reasonable possibilities for maintaining the stoichiometry of the decomposition of $Mn(C_2O_4)_2^-$ but no direct evidence for these steps appeared in Launer's[5] work. The above formulation of the mechanism for the catalysis of the reaction of chlorine and oxalic acid shows that if either manganous ion or chlorine is absent from the system, the trivalent manganese will not be regenerated after its reduction in step (1). The rapid disappearance of the substance under these conditions, and its conservation in the presence of divalent manganese and chlorine, thus find a simple explanation.

The data have yielded values for K_a, K_b, k_1, for the heat effect in reactions (a) and (b) and for the energy of activation of step (1). Several different ways of producing the catalyst in the system have been tested, and the effect of ferric ion on the net rate of decomposition of the catalyst studied and interpreted.

Experimental

Materials.—Hydrochloric acid and oxalic acid solutions were prepared from C. P. grades of chemicals dissolved in redistilled water. The solutions were treated with chlorine and were irradiated before use.

Mn(III) as the sulfate complex was prepared by adding manganese dioxide to a solution 6 *N* with respect to sulfuric acid and 0.1 *M* with respect to manganous sulfate, more manganous sulfate (in amount sufficient to increase the concentration to 0.2 *M*) being added to the solution containing the Mn(III) and Mn(II) after the excess manganese dioxide was removed by filtering.

Procedure.—A cell of the type previously employed[4] of volume 100 cc. was used in the present experiments, except that a simple stopper replaced the inducing agent buret. The required volumes of hydrochloric acid, manganous chloride and oxalic acid solutions were added, then after temperature equilibrium was established, a known volume of chlorine solution of known strength. Lastly, a measured small volume (usually 2 cc.) of the Mn(III) solution was added, with rapid stirring of cell contents during the process. Zero time was taken as the time at which the catalyst pipet was half emptied. After a chosen length of time had elapsed, the mixture was quenched by discharging it into a solution containing potassium iodide, and the final chlorine concentration was determined by titration. Thus in a single experiment at fixed conditions the change in concentration of chlorine and the time of reaction were the quantities measured.

Conditions.—The temperature was maintained at 25.2° in the majority of the experiments, 15.0 and 34.7° in others. The solutions were at ionic strength very nearly 2 in all cases. In all but a few experiments, the concentration of manganous ion was 0.01 *M*. The hydrochloric acid concentration was kept high, 2 *M* in most of the experiments, to minimize the spontaneous reaction[7] of chlorine and oxalic acid. The correction for this spontaneous reaction has been applied to all the data. Only in extreme cases was the correction in excess of 4% of the total effect. The correction due to the oxidation of iodide by the residual catalyst at the end of an experiment has been considered and applied where it was significant. The total catalyst added was, however, usually only about 2% of the change in chlorine concentration.

Definitions.—The time of reaction, *t*, is expressed in minutes, and the concentration in moles per liter throughout. Δ represents the change in the concentration of chlorine due to the catalyzed reaction of chlorine and oxalic acid. The total trivalent manganese concentration is represented by (Mn(III)), that of oxalate by (Oxalic). K_c refers to the quotient for the rapidly established equilibrium

$$H_2C_2O_4 = 2H^+ + C_2O_4^= \quad (C)$$

In the absence of measurements of K_c in 2 *M* hydrochloric acid, the value at zero ionic strength of 4×10^{-6} has been used. A 10-fold change in this value will not affect the conclusions which have involved its use.

Presentation of Data; Development of the Rate Law and Correlation with Mechanism

The Variation of Initial Rate with Chlorine and Oxalic Acid Concentration.—The data covering the variation of the rate of the reaction of chlorine and oxalic acid as a function of (Cl_2), (oxalic), (Mn(III)) and time of reaction are presented in Tables I and II. These data are discussed with reference to the rate law

$$-\,d(Cl_2)/dt = k(Mn(III))_0 \qquad I$$

using the corresponding integrated form

$$k = \Delta/(Mn(III))_0 t \qquad II$$

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[4] Taube, THIS JOURNAL, **68**, 611 (1946).

[5] Launer, *ibid.*, **54**, 2597 (1932).

[6] A complete piece of work on ferric ion–halide ion complexes is that of Rabinowitch and Stockmayer (THIS JOURNAL, **64**, 335, 1942); this paper contains references to earlier excellent work. A recent paper is that of Kossiakoff and Sickman, *ibid.*, **68**, 442 1946). Lanford and Kiehl, (*ibid.*, **64**, 291, 1942) have established the existence of $FeHPO_4^+$ in moderately acid solutions; this ion is closely analogous to the one postulated in the present paper.

[7] Griffith and McKeown, *Trans. Faraday Soc.*, **28**, 518 (1932).

The specific rate k calculated by equation II from the data will be a constant if the adopted mechanism operates, only if the net rate of decomposition of the catalyst is negligibly small, and if over the whole range of oxalic acid concentration, practically all the manganic ion added is present as the mono-oxalate complex.

It is evident from an examination of the data of Tables I and II that while k calculated by the above relation remains approximately constant over a considerable range of the variables, some important trends do occur. One of these trends is the decrease in k as the time of reaction increases. This variation is reserved for later discussion and for the time being attention will be directed to the values of k at time zero, when the reactants and the catalyst are still at the initial concentrations.

Figures 1 and 2 show the results of an analysis made to ascertain the values of k at zero time for each series of experiments with almost constant initial chlorine and oxalic acid concentration. In these figures k has been plotted against the product $(\text{Mn(III)})_0\, t$. A straight line has been directed through each series of points representing experiments at constant initial oxalic acid and chlorine concentration. The intercept of this line on the ordinate axis is accepted as k_0, the value of k at zero time for the particular series of experiments.

TABLE I

EXPERIMENTS AT LOW CHLORINE CONCENTRATION COVERING THE RANGE OF LOW OXALIC ACID CONCENTRATIONS

(HCl) = 2 M; (Mn^{++}) = 0.01 M except in expt. 1; temp. 25.2°

No.	t	$(\text{Oxalic})_0 \times 10^2$	$(\text{Cl}_2)_0 \times 10^2$	$\Delta \times 10^3$	$(\text{Mn(III)})_0 \times 10^4$	$(\text{Mn(III)})_0\, t \times 10^4$	k
1	5.05[a]	1.000	0.634	2.43	0.595	3.00	8.10
2	1.97	0.653	.645	.491	.272	0.535	9.20
3	6.05	.653	.635	1.420	.272	1.64	8.70
4	1.95	.500	.610	0.928	.525	1.025	9.05
5	2.03	.500	.676	.964	.525	1.065	9.05
6	2.03	.500	.660	.947	.525	1.065	8.90
7	4.00	.500	.650	1.79	.525	2.10	8.50
8	5.97	.500	.677	2.52	.525	3.14	8.00
9	6.03	.500	.632	2.60	.525	3.16	8.25
10	6.00	.500	.670	2.50	.525	3.15	7.95
11	1.50	.162	.620	0.310	.272	0.407	7.60
12	2.80	.162	.600	.556	.272	.761	7.30
13	1.46[b]	.131	.622	.277	.272	.397	7.00
14	3.00	.131	.610	.550	.272	.815	6.75
15	1.47	.0970	.605	.232	.272	.400	5.80
16	1.46[c]	.0645	.612	.196	.272	.397	4.95
17	3.00	.0645	.610	.385	.272	.815	4.70
18	1.50[b]	.0323	.600	.118	.272	.408	2.9
19	1.50	.0161	.605	.066	.272	.408	1.6

[a] (Mn^{++}) = 0.002 M. [b] Mean of two experiments. [c] Mean of three experiments.

TABLE II

EXPERIMENTS AT HIGHER CHLORINE CONCENTRATION COVERING THE RANGE OF HIGH VALUES OF OXALIC ACID CONCENTRATION

(HCl) = 2 M; (Mn^{++}) = 0.01 M; temp., 25.2°

No.	t	$(\text{Oxalic})_0 \times 10^2$	$(\text{Cl})_0 \times 10^2$	$\Delta \times 10^3$	$(\text{Mn(III)})_0 \times 10^4$	$(\text{Mn(III)})_0\, t \times 10^4$	k
1	6.20	0.25	1.57	1.62	0.308	1.91	8.50
2	6.13	.50	1.54	1.72	.305	1.87	9.20
3	6.20	1.00	1.57	1.80	.313	1.94	9.25
4	6.25	1.00	1.54	1.95	.337	2.11	9.25
5	6.20	1.00	1.53	3.52	.644	3.99	8.80
6	6.30	1.00	1.54	3.48	.636	4.00	8.70
7	6.16	1.00	1.57	5.34	1.030	6.35	8.40
8	6.20	1.00	1.52	6.00	1.197	7.42	8.10
9	3.10	2.00	1.63	2.30	0.835	2.59	8.90
10	6.20	2.00	1.62	4.40	.840	5.21	8.45
11	12.15	2.00	1.52	8.34	.856	10.40	8.00
12	6.83	2.00	1.52	2.14	.353	2.41	8.90
13	6.15	2.00	1.51	3.20	.612	3.76	8.50
14	6.20	2.00	1.60	3.48	.644	3.99	8.72
15	6.25	2.00	1.45	5.36	1.030	6.45	8.30
16	6.32	2.00	1.63	5.50	1.06	6.70	8.20
17	6.25	2.00	1.52	7.30	1.49	9.31	7.85
18	6.10	4.02	1.66	1.54	0.326	1.99	7.75
19	6.10	3.98	1.67	2.96	.648	3.96	7.50
20	6.30	3.94	1.57	4.97	1.091	6.88	7.25
21	12.10	3.98	1.57	5.70	0.656	7.95	7.15
22	6.20	3.94	1.61	8.65	2.01	12.45	6.95
23	19.25	3.98	1.57	8.65	0.664	12.78	6.80
24	6.20	7.95	1.55	4.07	1.152	7.15	5.70
25	6.20	15.90	1.63	3.40	1.355	8.40	4.05
26	2.95	1.97	3.16	3.84	1.46	4.31	8.90
27	3.60	1.97	2.98	4.64	1.46	5.26	8.90
28	8.05	1.97	3.16	10.05	1.46	11.75	8.55
29	8.00	1.97	3.17	9.95	1.46	11.70	8.50

Figure 3 presents the values of k_0 thus obtained plotted against log (oxalic) for three different concentrations of chlorine. In several cases, k for given chlorine and oxalic acid concentration was measured only for a single value of $(\text{Mn(III)})_0 t$ (see Tables I and II). In these cases, k_0 was obtained by directing through the single point a line at a slope suggested by adjacent experimentally established lines. The results presented in Fig. 3 show, as is indicated also by comparisons in Tables I and II, that k_0 is independent of the concentration of chlorine over the range investigated, a behavior which is consistent with the postulated mechanism for reaction. A second feature of interest is that k_0 does vary with the concentration of oxalic acid, decreasing both at high and at low values of oxalic acid concentration.

The most straightforward explanation for the variation of k_0 with the oxalic acid concentration is that the degree of complexing by oxalate of trivalent manganese changes as the concentration

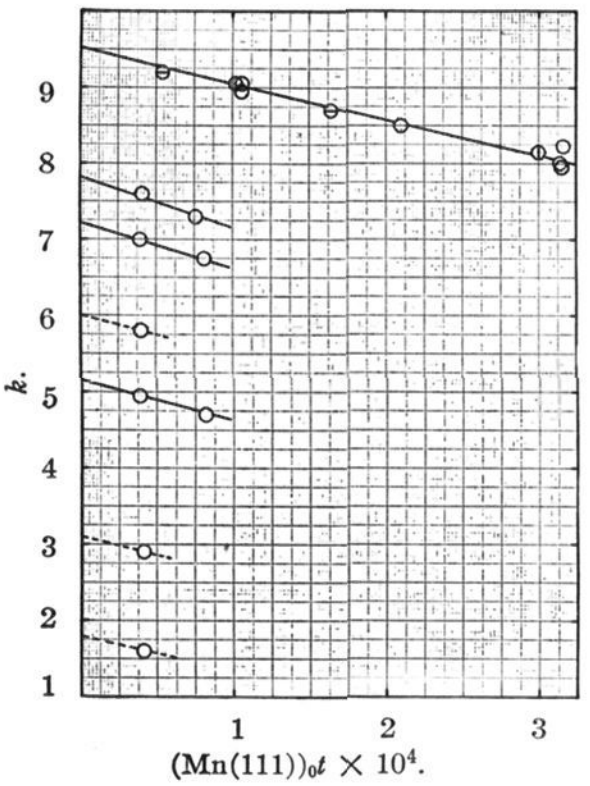

Fig. 1.—Determination of the initial specific rates of reaction at low oxalic acid concentration. Data taken from Table I. (Cl_2) is *ca.* 6.4×10^{-3} *M*. (Oxalic)$_0$ for lines numbered in order from the top: 1, ⦶ 10×10^{-3} *M*, ⊖ 6.53×10^{-3} *M*, ○ 5×10^{-3} *M*; 2, 1.62×10^{-3} *M*; 3, 1.31×10^{-3} *M*; 4, 0.97×10^{-3} *M*; 5, 0.645×10^{-3} *M*; 6, 0.323×10^{-3} *M*; 7, 0.161×10^{-3} *M*.

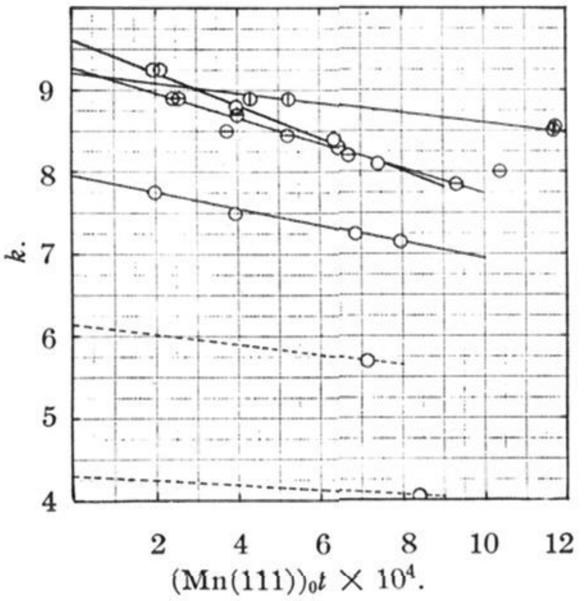

Fig. 2.—Determination of the initial specific rates at high oxalic acid concentration. Data taken from Table II. Lines are counted in order of decreasing intercept on the vertical axis. (Cl_2)$_0$ is everywhere *ca.* 1.55×10^{-2} *M* except for line 3 where it is 3.1×10^{-2} *M*. (Oxalic)$_0$ for each series as follows: 1, 1.0×10^{-2} *M*; 2, 2.0×10^{-2} *M*; 3, 1.97×10^{-2} *M*; 4, 4.0×10^{-2} *M*; 5, 7.95×10^{-2} *M*; 6, 15.9×10^{-2} *M*.

of oxalic acid changes. In an intermediate range of oxalic acid concentration most of the trivalent manganese may be present as the labile ion $MnC_2O_4^+$, and in this region a maximum value for k_0 is expected. At high oxalic acid, the $MnC_2O_4^+$ concentration, and thus the rate will be

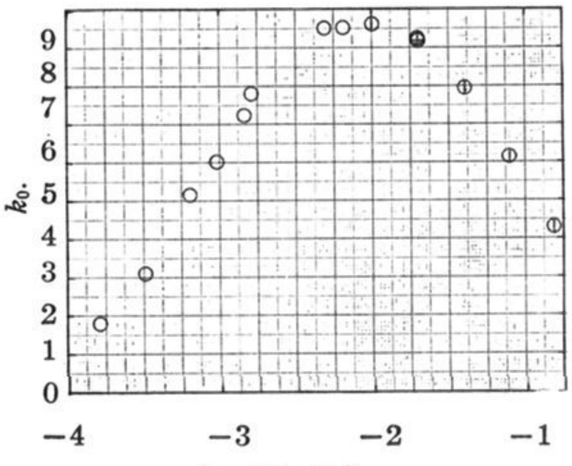

Fig. 3.—The variation of the initial specific rates with the concentration of oxalic acid at several concentrations of chlorine: ○, *ca.* 6.4×10^{-3} *M* Cl_2; ⦶, *ca.* 1.55×10^{-2} *M* Cl_2; ⊖, *ca.* 3.1×10^{-2} *M* Cl_2.

reduced by the partial conversion of $MnC_2O_4^+$ to $Mn(C_2O_4)_2^-$ (equilibrium b) and at low oxalic acid by conversion to Mn_{Cl}^{+++} (equilibrium a). A quantitative test of this interpretation is to discover whether the data are consistent with constant values for the equilibrium quotients governing the equilibria (a) and (b) and for k_1 the specific rate of reaction (1). If k_1 is known, K_a and K_b can be calculated by applying the relation[8] $K_a = k_0(H^+)^2/(k_1 - k_0)(H_2C_2O_4)$ and $K_b = (k_1 - k_0)(H^+)^2/k_0(H_2C_2O_4)$ to the results at low and at high values of oxalic acid concentrations, respectively. In the equation for K_a, $k_0/(k_1 - k_0) = (MnC_2O_4^+)/(Mn_{Cl}^{+++})$ and in the equation for K_b, $(k_1 - k_0)/k_0 = (Mn(C_2O_4)_2^-)/(MnC_2O_4^+)$. With k_1 chosen equal to 11.4 min.$^{-1}$ for the conditions obtaining in the experiments of Tables I and II, values of K_a and K_b as shown in Table III are calculated from the data. The reasonable constancy of the values of K_a and K_b for constant k_1 seem to establish as sound the interpretation given to the results. While the assumption of Mn_{Cl}^{+++} and $Mn(C_2O_4)_2^-$ as the only important

TABLE III

DETERMINATION OF THE ASSOCIATION CONSTANTS K_a AND K_b AT 25.2° IN 2 *M* HCl

k_0	$(H_2C_2O_4)_0{}^a \times 10^3$	$K_a \times 10^{-3}$	k_0	$(H_2C_2O_4)_0{}^a \times 10^3$	K_b
	Low (oxalic)			High (oxalic)	
7.8	1.57	(5.8)	9.2	19.4	(41)
7.2	1.27	5.5	7.95	38.8	43
6.0	0.93	4.9	6.15	77.1	45
5.15	.613	5.4	4.3	154	43
3.1	.303	4.9			
1.8	1.57	4.9			
	Mean = 5.1×10^3			Mean = 44	

[a] These are calculated from the known values of hydrochloric acid concentration and of (oxalic), using for the first acid dissociation constant of oxalic acid the value 0.06, and are corrected for the oxalic acid consumed in association with Mn^{+++}.

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(8) A small correction is necessary in each range for the contribution by the other equilibrium. This has been applied to the values reported in Table III.

species will explain qualitatively the observed variation of k_0 with $(H_2C_2O_4)$, the data cannot be interpreted quantitatively in this manner.

Direct visual observations support the conclusions about the degree of complexing by oxalate of trivalent manganese. If to a series of three solutions each about 0.02 M in chlorine, 2 M in hydrochloric acid and 0.01 M in Mn^{++}, and in order 0, 0.01, 0.3 M with respect to oxalic acid, Mn(III) is added, (final concentration about $2 \times 10^{-4}M$) the following comparison of colors can be made. The first solution is pale yellow, the second has a deeper and cherry red color, while the third has a golden yellow to orange color. On the basis of the equilibrium quotients presented, the first will contain mainly the complex with chloride ion, the second chiefly $MnC_2O_4^+$ and the third chiefly $Mn(C_2O_4)_2^-$. The mangani dioxalate complex has been described by Cartledge and Ericks[9] as golden yellow in color. Measurements by the same authors of the equilibrium between the dioxalate and trioxalate complexes make it seem unlikely that the trioxalate complex is an important species in the solutions under investigation.

The Effect of Acid Concentration.—A few experiments were devoted to a study of the effect of varying the concentration of hydrogen ion at constant ionic strength. The results of these experiments are presented in Table IV.

TABLE IV

THE EFFECT OF VARYING CONCENTRATION OF HYDROGEN ION. (HCl) = 1 M; (KCl) = 1 M; (Mn^{+++}) = 0.01 M; TEMP. = 25.2°

No.	t	$(\text{Oxalic})_0 \times 10^2$	$(Cl_2)_0 \times 10^2$	$\Delta \times 10^3$	$(Mn(III))_0 \times t \times 10^4$	k	k_0
1	6.15	1.0	1.66	3.52	5.17	6.80	
2	6.22	1.0	1.59	1.78	2.56	6.95	7.10
3	5.00	0.30	0.66	2.30	3.00	7.80	
4	2.50	.30	.70	1.22	1.50	8.50	9.25

The results reported in Table IV are of interest in comparison with experiments 3 to 8 of Table II and experiments 2 to 10 of Table I. It is noted that when the oxalic acid concentration is at 0.01 M, a decrease in the concentration of hydrogen ion at constant ionic strength results in a decrease in k_0; however, if the concentration of oxalic acid is also reduced k_0 rises to values equal to the maximum values at higher acidity. These results are understood if a change in acid concentration affects the degree of complexing of the trivalent manganese, but does not affect the specific rate of decomposition of $MnC_2O_4^+$.[10] On this basis at 0.01 M oxalic acid in 1 M hydrochloric acid a substantial fraction of the catalyst is converted into the higher complex. Using for k_1 a value of 11.4 also at 1 M hydrochloric acid and 1 M potassium chloride, K_b for these conditions is calculated to be 62. The comparison with the corresponding value of 44 in 2 M hydrochloric acid is consistent with the formulation of the equilibrium concerned as (b) (see Introduction). The discrepancy in the values is probably due to specific effects of hydrochloric acid and potassium chloride on the activity coefficients of the substances involved in the equilibrium.

The Variation of the Rate of Reaction with the Concentration of Manganous Ion.—If the concentration of manganous ion is low atomic chlorine will disappear principally by recombination[4] to form molecular chlorine, rather than reaction by step 6 to regenerate the trivalent manganese. Under these conditions, the lifetime of the catalyst is short and its catalytic activity is almost unnoticeable. However, as the concentration of manganous ion is increased, a greater and greater fraction of the manganic ion reduced in step 1 is regenerated by step 6. When the concentration of manganous ion is sufficiently great to consume substantially all of the atomic chlorine, increasing the concentration will exert no further effect on the rate of the main reaction or on the lifetime of the catalyst. That the experiments reported have been carried out in this region of "saturation" with respect to manganous ion is shown by the result obtained in experiment 1 of Table I. In this experiment the concentration of manganous ion was only one fifth of that commonly employed but the rate of reaction did not differ appreciably from that observed in experiments similar in other respects.[11] However, if the concentration of manganous ion is further reduced by a factor of two, the value of k does decrease by about 5% (experiment not reported).

The following considerations show that at 0.01 M manganous ion in the experiments under discussion, the rate of reaction 6 is expected to be very large compared to the rate of recombination of atomic chlorine

$$Cl + Cl \xrightarrow{k_5} Cl_2 \qquad (5)$$

If steps 5 and 6 compete for the net consumption of atomic chlorine, and the rates of 7 and 8 remain small, the following relation will hold

$$k_5(Cl)^2 + k_6(Mn^{++})(Cl) = k(Mn(III)).$$

If in the above equation, k_6[12] is replaced by $\sqrt{k_5} \times 1300$, (Mn^{++}) by its usual value of 0.01 M, k by its usual value of about 9, and (Mn(III)) by the maximum value employed, 2×10^{-4} M, on solving the equation $\sqrt{k_5}(Cl)$ is found to be 1.4×10^{-4}. Path 5 therefore compares to path 6 as $(1.4 \times 10^{-4})^2$ compares to $1300 \times 0.01 \times 1.4 \times 10^{-4}$, and therefore only about 10^{-3}% or less of the atomic chlorine recombines under the conditions of most of the experiments.

Similar considerations based on previous work[4]

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[9] Cartledge and Ericks, THIS JOURNAL, **58**, 2065 (1936).

[10] Ref. 5, p. 2602.

[11] Since the rate of reaction is not markedly dependent on oxalic acid concentration in the range under consideration, the comparison of experiment 1 with experiments 8 to 10 is valid.

[12] k_6 has been shown to be about 1300 under the present conditions $k_6/\sqrt{k_5}$ (ref. 5).

show that the reactions of atomic chlorine with oxalic acid or the oxalate free radical are not important processes for atomic chlorine when the manganous ion concentration is high.

The Mechanism of Destruction of the Catalyst.—It can be established by direct visual observation that as time increases, the concentration of Mn(III) in the solutions under study decreases. In this section it will be shown that if this net consumption is assumed to proceed by way of the reactions (7) and (8), the observed decrease of *k* (Fig. 1 and 2) with increasing values of $(\mathrm{Mn(III)})_0t$ finds a complete explanation.

It can be shown that the mechanism including reactions (7) and (8) leads to equation (III) below if the three conditions are fulfilled: that a steady state with respect to chlorine and the reducing intermediate is rapidly reached, that the rate of consumption of chlorine and oxalic acid is much in excess of the net rate of consumption of the catalyst, and that the fractional change in catalyst concentration is low. Of these conditions, the third is least stringently fulfilled in the experiments.

$$\frac{\Delta}{(\mathrm{Mn(III)})_0t} = k = k_1F - (k_1F)^2\frac{k_7'(\mathrm{Mn(III)})_0t}{k_3(\mathrm{Cl_2})} \qquad \text{(III)}$$

In equation (III)

$$F = 1\Big/\left[\frac{(\mathrm{H^+})^2}{K_\mathrm{a}(\mathrm{H_2C_2O_4})} + 1 + \frac{(\mathrm{H_2C_2O_4})K_\mathrm{b}}{(\mathrm{H^+})^2}\right]$$

and

$$k_7'/k_3 = \frac{k_7}{k_3} + \frac{k_8}{k_3}\frac{(\mathrm{H^+})^2}{(\mathrm{H_2C_2O_4})}$$

The first term in equation III is the value of *k* at $t = 0$, and is therefore to be identified with k_0 discussed above. *F* is the function which expresses the effect, discussed in an earlier section, of the change in the state of complexing of Mn(III) by oxalate, on the rate of the main reaction.

The second term of equation III expresses the effect on *k* of the progressive loss with time of the catalyst Mn(III). k_7'/k_3 is composed of two terms, to account for the reaction of the reducing intermediate with $\mathrm{MnC_2O_4^+}$ and with $\mathrm{MnCl^{+++}}$. The data did not require a third term representing the reaction with $\mathrm{Mn(C_2O_4)_2^-}$; if this reaction does proceed, its specific rate is considerably lower than those of steps (7) and (8).

It can readily be seen that equation III describes the general features of the data of Fig. 1 and 2. Attention is directed to the fact that for constant oxalic acid concentration, the slopes of the lines in Figs. 1 and 2 are expected from this equation to vary inversely as $(\mathrm{Cl_2})$, and that at fixed $(\mathrm{Cl_2})$ and $(\mathrm{H_2C_2O_4})$, *k* is expected to be a function of the product $\mathrm{Mn(III)}_0t$. Particularly interesting in this connection are the results of experiments 22 and 23 in Table II; while the values of $(\mathrm{Mn(III)})_0$ and *t* are quite different in these experiments, their products are equal, and very nearly equal values of *k* are observed.

In Table V, the results of a test of the equation, choosing the data of Figs. 1 and 2 for the region of fairly high oxalic concentration (where reaction 8 contributes only a little) are presented.

TABLE V

THE TEST OF THE MECHANISM FOR THE NET DECOMPOSITION OF THE CATALYST AT RELATIVELY HIGH OXALIC ACID CONCENTRATION

(HCl) = 2 *M*; temp. = 25.2°

$(\mathrm{Oxalic})_0 \times 10^3$	$(\mathrm{Cl_2})_0 \times 10^3$	k_1F	k_7'/k_3[a]	k_7/k_3[a]
5.0	6.4	9.5	0.33	0.22
10.0	15.4	9.6	.31	.25
20.0	15.5	9.3	.27	.24
39.5	15.8	7.9	.25	.24
19.7	31.5	9.2	.24	.21

[a] k_7'/k_3 are the values calculated directly from the slopes of the lines in Figs. 1 and 2. The values for k_7/k_3 are obtained by correcting for the contribution by reaction 8, using for k_8/k_3 at 25.2° the same value as at 34.7°, namely, 0.7 (see below).

The data at high $(\mathrm{H_2C_2O_4})$ cover a range eight-fold in $(\mathrm{H_2C_2O_4})$, and five-fold in chlorine concentration and are seen to conform fairly well to equation III. Since small variations in *k* produce highly magnified changes in the slopes of the lines which yield the values of k_7/k_3, a possible experimental error in these values of as much as 20% must be admitted. The treatment of the data is in any case approximate, since the concentration of chlorine is not constant in a series; beyond random initial variations there is a gradual decrease in the chlorine concentrations as $(\mathrm{Mn(III)})_0t$ increases. However, in spite of the inaccuracies, the data seem to fix k_7/k_3 at about 0.23 ± 0.05 at 25.2°.

The data at 25.2° were not sufficiently extensive or accurate to test the rate law at low values of $(\mathrm{H_2C_2O_4})$ and the data at 34.7°, in most cases representing a mean of two or three experiments, were used. The pertinent experiments are reported in Table VI, the numbers there being those assigned in Table VII. Applying Equation III, values for k_7'/k_3 are calculated from each experiment, using the average values for $(\mathrm{Cl_2})$ and $(\mathrm{H_2C_2O_4})$ in each experiment, and for K_a, k_1 and k_7/k_3 at 34.7°, 6.7×10^3, 28.8, and 0.21, respectively (see below).

TABLE VI

THE DECREASE OF *k* WITH TIME AT LOW OXALIC ACID CONCENTRATION. TEMPERATURE 34.7°

(HCl) = 2 *M*; $k' = 28.8$; $K_a = 6.7 \times 10^3$; $k_7/k_3 = 0.21$

No.	$(\mathrm{H_2C_2O_4}) \times 10^4$	$(\mathrm{Cl_2}) \times 10^3$	k	k_1F	k_7'/k_3	k_8/k_3
16	12.3	4.3	18.1	19.5	0.42	(0.45)
17	12.5	3.8	17.6	19.3	0.43	(.45)
19	4.1	4.4	10.2	11.7	1.1	.7
21	2.0	4.7	6.2	7.2	2.4	.7

The drift of the values of k_7'/k_3 with $(\mathrm{H_2C_2O_4})$ reveals the necessity for including reaction 8 in the mechanism. At high $(\mathrm{H_2C_2O_4})$ as in experiments 16 and 17, the contribution by this step is small and the values of k_8/k_3 here are considerably less accurate than those at lower ($H_2C_2O_4$). In any case no great accuracy can be claimed for these values, and the comparison of k_7/k_3 and k_8/k_3 will serve only to show that the reducing intermediate reacts less rapidly with $MnC_2O_4^+$ than with Mn_{Cl}^{+++}.

The Temperature Coefficients of the Equilibrium Constants and of the Specific Rates.— The results of experiments performed at 34.7° are reported in Table VII. In Figs. 4 and 5 these data are subjected to the analysis employed above to establish the values of k_0. When plotted against the concentration of oxalic acid, k_0 is observed as at 25.2°, to be maximum for an intermediate range of oxalic acid concentrations. In this case, however, the high values extend both to higher and to lower oxalic acid concentrations thus indicating, as the comparison of K_a and K_b at various temperatures will express quantitatively, that both Mn_{Cl}^{+++} and $Mn(C_2O_4)_2^-$ decrease relative to $MnC_2O_4^+$ as the temperature rises.

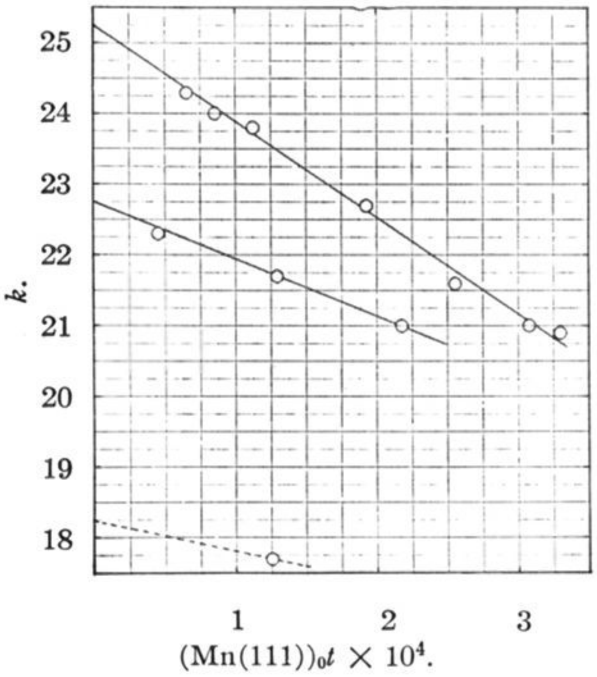

Fig. 4.—The determination of the initial specific rates of reaction at 34.7° for relatively high values of (Oxalic)₀. (Cl_2)₀ is *ca.* 1.1 × 10^{-3} *M*. Data are taken from Table VII. (Oxalic)₀ for lines numbered in order from the top: 1, 2.00 × 10^{-2} *M;* 2, 4.04 × 10^{-2} *M;* 3, 8.1 × 10^{-2} *M*.

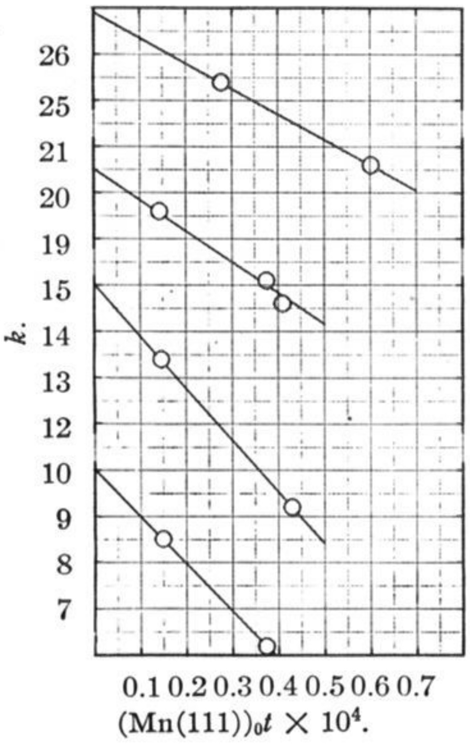

Fig. 5.—The determination of the initial specific rate of reaction at 34.7° for relatively low values of (Oxalic)₀. Data taken from Table VII. (Cl_2)₀ is *ca.* 4.6 × 10^{-3} *M*. (Oxalic)₀ for lines counted in order from top to bottom as follows: 1, 8.1 × 10^{-3} *M;* 2, 1.16 × 10^{-3} *M;* 3, 0.645 × 10^{-3} *M;* 4, 0.322 × 10^{-3} *M*.

TABLE VII

RESULTS OF EXPERIMENTS AT 34.7°

(HCl) = 2 *M;* (Mn^{++}) = 0.01 *M*

No.	*t*	(Oxalic)₀ × 10³	(Cl_2)₀ × 10³	Δ × 10³	(Mn (III))₀ × 10⁴	(Mn (III))₀ *t* × 10⁴	*k*
1	4.60	81.0	10.6	2.21	0.272	1.25	17.7
2[a]	1.69	40.4	10.4	1.025	.272	0.460	22.3
3	4.79	40.4	10.3	2.82	.272	1.30	21.7
4	8.00	40.4	11.2	4.58	.272	2.18	21.0
5	2.40	20.2	10.9	1.585	.272	0.653	24.3
6	1.60	20.0	11.4	2.06	.535	.856	24.0
7	2.10	20.0	11.4	2.70	.539	1.13	23.8
8	3.60	20.0	10.7	4.38	.535	1.93	22.7
9	4.80	20.0	11.1	5.54	.535	2.56	21.6
10	2.70	20.0	11.0	6.46	1.140	3.08	21.0
11	6.15	20.0	12.3	6.91	0.537	3.30	20.9
12	2.23	8.10	10.1	1.535	.272	0.606	25.3
13	2.56	8.10	4.4	0.712	.109	.280	25.4
14	5.53	8.10	4.6	1.420	.109	.603	23.6
15[b]	1.30	1.61	4.7	0.278	.109	.142	19.6
16	3.45	1.61	4.65	.680	.109	.376	18.1
17	3.76	1.61	4.20	.722	.109	.410	17.6
18	1.36	0.645	4.5	.198	.109	.148	13.4
19[a]	3.95	.645	4.6	.440	.109	.431	10.2
20	1.38	.322	4.7	1.27	.109	.150	8.5
21[a]	3.43	.322	4.8	.230	.109	.374	6.2

[a] Mean of two experiments. [b] Mean of three experiments.

In Table VIII it is shown that the data on the variation of k_0 with the concentration of oxalic acid at 34.7° are consistent with values for k_1, K_a and K_b at that temperature of 28.8 min.$^{-1}$, 6.7 × 10^3 and 28.5.

TABLE VIII

DETERMINATION OF K_a AND K_b AT 34.7°

(k_1 at 34.7° is chosen as 28.8 min.$^{-1}$)

Low (oxalic)			High (oxalic)		
($H_2C_2O_4$)₀ × 10	k_0	Ka × 10⁻³	($H_2C_2O_4$) × 10	k_0	K_b
1.56	20.5	6.5	78.6	18.25	29
0.625	15.0	6.8	39.2	22.75	26
0.313	10.0	6.8	19.6	25.25	29
Mean value K_a = 6.7 × 10³			Mean value K_b = 28		

Experiments at 15.0° were also performed, and the results of analysis of the data to establish k_1, K_a and K_b at that temperature are recorded in

Table IX. Column 2 gives the experimental values of k_0; these differed only slightly from the measured values of k since at 15° the trend with time is not very marked. K_a, K_b and k_0 were determined by finding for them the combination of values which would best reproduce k_0 observed, using the relation $k_0 = k_1 F$.[13] When K_a, K_b and k_1 are chosen as 3.2×10^3, 74 and 3.52, respectively, the values of k_0 calculated compare with the experimental as shown in Table IX. The fit is satisfactory but the data are not extensive enough to fix the individual parameters with great exactness. k_0 is most sensitive to change in k_1 and of the three constants to be determined k_1 is fixed most exactly by the data.

TABLE IX

DETERMINATION OF k_1, K_a AND K_b AT 15°

$(HCl) = 2\ M$, $(Cl_2)_0 = 9 \times 10^{-3}\ M$, $(Mn^{++}) = 0.01\ M$

See text for definition of k_0 calcd.

$(H_2C_2O_4) \times 10^3$	k_0 exp.	k_0 (calcd.)
2.91	2.37	2.37
4.85	2.60	2.61
9.60	2.67	2.69
19.4	2.48	2.48

In Fig. 6 the logarithms of the values of k_1, K_a and K_b are plotted against the reciprocal of the temperature. From the slopes of the lines drawn through the series of points the following heat effects are calculated: for the activation energy of step 1, 18,300 ± 500 cal.; for ΔH in reaction (a), +6,000 ± 1500 cal.; and ΔH in reaction (b), −8700 ± 1000 cal.

The series of experiments at 34.7° with the concentration of oxalic acid at 0.02 M yields for k_7/k_3 a value of 0.21. From the comparison with the value 0.23 obtained at 25.2° the conclusion can be drawn that the activation energies of reactions 3 and 7 are nearly the same. Unless widely different pz factors for steps 3 and 7 are accepted, the observation that the activation energies are nearly the same follows already from the fact that the specific rates k_7 and k_3 differ by only a small factor.

Summary of Rate Law Data.—Following are the values in 2 M hydrochloric acid for three temperatures of the several specific rates, specific rate ratios and equilibrium quotients which appear in the equation III.

	At 15.0°	At 25.2°	At 34.7°
k_1	3.52 min.$^{-1}$	11.4 min.$^{-1}$	28.8 min.$^{-1}$
k_7/k_3	....	0.23	0.21
k_8/k_3	....	(0.7)	0.7
K_a	3.2×10^3	5.1×10^3	6.7×10^3
K_b	74	44	28.5

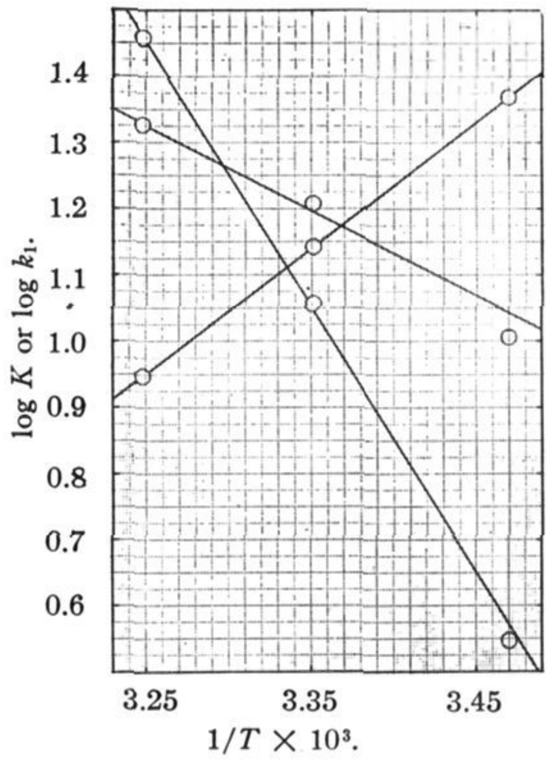

Fig. 6.—The variation of k_1, K_a and K_b with temperature. Lines are counted in order of decreasing intercept on the vertical axis: 1 represents values of k_1; 2, values of K_a; 3, values of K_b. The origin for the vertical axis is arbitrarily chosen.

Production of Mn(III) in the Solutions by Various Means.—To prove that the effects observed are not specific for the particular complex of trivalent manganese added, experiments were carried out adding other oxidizing agents to a solution containing chlorine, oxalic acid, hydrochloric acid and manganous ion. Cobaltic and ceric ions were found to give quantitatively the same effect as if an equivalent amount of Mn(III) had been added. If the oxalic acid concentration is not too high cobaltic and ceric ion are reduced almost as rapidly as they are added. Whether the mechanism of reduction is by direct oxidation of manganous ion or by the primary oxidation of oxalic acid is not established by these experiments, but the experiments do establish that net result of the reactions is the production of Mn(III) equivalent to the cobaltic and ceric ion added. Permanganate ion was also observed to give almost quantitatively the same effect, the slight difference being attributable to its noticeably slow reduction in the system.

It was also shown that Mn(III) can be built up in the system by exposing a solution containing chlorine, oxalic acid, hydrochloric acid and manganous ion to a strong source of light. This effect of light is also expected from the mechanism, the light being a simple means of producing atomic chlorine in the system. The concentration of Mn(III) which can thus be built up is sufficiently high to impart color to the solution.

The Effect of Ferric Ion and Other Substances.—Ferric ion does not oxidize Mn^{++} to Mn(III) under the experimental conditions, nor does it oxidize oxalic acid at an appreciable rate. The possibility exists, however, that it may react rapidly with the reducing intermediate; if then the ferrous ion thereby formed is oxidized more rapidly by Mn(III) than by chlorine, the effect

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(13) See Equation III.

exerted by ferric ion will be to enhance the net rate of disappearance of Mn(III). Visual observations have established this for ferric ion. The effect has also been studied quantitatively, measuring the rate of the chlorine–oxalic acid reaction catalyzed by Mn(III) in the presence of ferric ion, at varying concentrations of ferric ion and of chlorine, oxalic acid and Mn(III). Analysis of the data shows that the effect can be described by the reactions

$$\mathrm{Fe(III)} + \mathrm{C_2O_4^-} \xrightarrow{k_9} \mathrm{Fe^{++}} + 2\mathrm{CO_2} \qquad (9)$$

$$\mathrm{Fe^{++}} + \mathrm{Mn(III)} = \mathrm{Fe(III)} + \mathrm{Mn^{++}} \text{ (rapid)}$$

and that the value of k_9/k_3 at 25.2° when ($H_2C_2O_4$) is 0.005 *M* is *ca.* 0.19. The values calculated from the data show a drift indicating that ferrous ion is to some extent oxidized also by chlorine, but the ratio k_9/k_3 does not depend markedly on the concentration of oxalic acid in the range 0.005 to 0.010 *M*. 0.19 is to be regarded as a lower limit for k_9/k_3 but probably not far removed from the actual value.

In experiments performed under comparable conditions, Cu^{++} and Ti(IV) were observed to exert no noticeable effect on the rate of reaction. Oxygen at the pressure prevailing in the atmosphere and under the present conditions is without noticeable influence on the rate of the main reaction or on the rate of net decomposition of the catalyst.

General Discussion

The results which have been presented seem sufficiently extensive and consistent to establish that in the system under study, the rate of reaction of chlorine and oxalic acid is governed by the rate of oxidation of oxalic acid by trivalent manganese, that the reactivity of the catalyst is affected by its degree of complexing with oxalate, and that the catalyst undergoes net consumption by reaction with some reducing intermediate present in the system. These general conclusions do not lead directly to the detailed steps proposed, and for the mechanism to be acceptable the elimination of other chemically reasonable possibilities is required.

One of these possibilities is that step (1′), a bimolecular reaction of Mn^{+++} and $C_2O_4^=$ is the slow initial step, rather than the step (1), a monomolecular decomposition of the ion $MnC_2O_4^+$. The forms of the rate laws for both steps are identical except that k_1 must be replaced by $k_1'K_c/K_a$ if (1′) is adopted in place of (1). The following arguments, however, seem to make step (1′) an unlikely possibility. From the equality $k_1' = k_1'K_c/K_a$, k_1' would have a value of the order of 10^{10}. The activation energy of step (1′) would be in excess of the over-all activation energy of 18,300, since the heat effect in equilibrium (c) is small,[14] and does not compensate completely for the contribution to the over-all activation energy of the equilibrium (a). To make the specific rate of 10^{10} compatible with an activation energy of 18,300 cal. or higher, a *pz* factor of 10^{23} or greater would be necessary. Since this is outside the range of possible values, it seems unlikely that step (1′) operates under the present conditions.

Interpreting the rate determining step to be a monomolecular decomposition of $MnC_2O_4^+$, as is done in step (1), requires the frequency factor for this change to be about 2×10^{14} min.$^{-1}$, which is in the range of reasonable values for monomolecular reactions.

An ambiguity also exists with respect to the identity of the products of the rate determining step 1. The steps

$$\mathrm{MnC_2O_4^+} \longrightarrow \mathrm{Mn^+} + 2\mathrm{CO_2} \qquad (1'')$$

$$\mathrm{Mn^+} + \mathrm{Cl_2} = \mathrm{Mn^{++}} + \mathrm{Cl} + \mathrm{Cl^-} \qquad (3')$$

$$\mathrm{Mn^{++}} + \mathrm{Cl} = \mathrm{Mn^{+++}} + \mathrm{Cl^-} \qquad (6)$$

$$\mathrm{Mn^+} + \mathrm{MnC_2O_4^+} \longrightarrow 2\mathrm{Mn^{++}} + \mathrm{C_2O_4^=} \qquad (7')$$

together with the equilibria (a) and (b) fit the requirements of the rate law as well as the mechanism adopted. In this alternative scheme for reaction, the reducing intermediate is Mn^+, whereas in the formulation used as a basis for discussion of the data it is $C_2O_4^-$. An effort to reach a definite decision between the two mechanisms by comparing the effect of ferric ion in the present system, to that which it may exert in a similar system involving Ce^{+4} and Ce^{+3} for example, is at present being made. If $C_2O_4^-$ is common to both systems, and if ferric ion exerts an influence only by reaction with $C_2O_4^-$, the effect of ferric ion in both systems should compare quantitatively.

Among the conclusions of interest in the present work are those concerned with the degree of complexing of trivalent manganese and oxalate. The data at 25° are summarized as follows

$$\mathrm{H_2C_2O_4} + \mathrm{Mn_{Cl}}^{+++} = \mathrm{MnC_2O_4^+} + 2\mathrm{H^+} \qquad \text{(a)}$$

$$K_a = 5.1 \times 10^3,\ \Delta H = 6{,}000,\ \Delta F = -5{,}100,\ \Delta S = 37$$

$$\mathrm{MnC_2O_4^+} + \mathrm{H_2C_2O_4} = \mathrm{Mn(C_2O_4)_2^-} + 2\mathrm{H^+} \qquad \text{(b)}$$

$$K_b = 44,\ \Delta H = -8{,}700,\ \Delta F = -2{,}200,\ \Delta S = -22$$

The free energy, enthalpy and entropy changes refer in each case to the transformation to products of 1 mole of the ion for the prevailing environment—2 *M* hydrochloric acid.

An unsatisfactory feature of the results is that the degree of complexing of chloride ion with the various trivalent manganese species is unknown. Consideration of the entropy and enthalpy data leads to some general conclusions about this aspect of the problem. It is difficult to reconcile the observation that reaction (a) is endothermic while reaction (b) is exothermic unless it is assumed that step (a) involves replacement of chloride ion by oxalate rather than direct attachment of oxalate ion. That interaction of chloride ion and Mn^{+++} is strong follows also from the known fact that even fairly weak oxidizing agents oxidize Mn(II) to Mn(III) in the presence of hydrochloric acid

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(14) The heat of complete neutralization per mole of oxalic acid is 28,300 cal. (Landolt-Börnstein, "Tabellen").

at high concentration. However, the observation that the entropy change of reaction (a) has a large positive value seems to require that there be a substantial reduction of charge of the complex ion when reaction (a) takes place. An acceptable formulation for the principal equilibrium on the basis of these arguments would be

$$MnCl^{+++} + H_2C_2O_4 = MnC_2O_4^+ + 2H^+ + Cl^-$$

but other possibilities, involving mixed complexes would also meet the requirements.

Among the data from the present work which may have applications to other systems are those dealing with the relative specific rate of reaction of the reducing intermediate, CO_2^-, $C_2O_4^-$ or Mn^+, with several oxidizing agents. These relative specific rates of reaction are summarized below

Cl_2	Mn_{Cl}^{+++}	$MnC_2O_4^+$	Fe(III)	$Mn(C_2O_4)_2^-$
k_3	$0.7\ k_3$	$0.23\ k_3$	*ca.* $0.19\ k_3$	$\ll k_3$

Of interest is the comparison among the three manganese complexes, particularly the monooxalato with the dioxalato complex, the specific rate of reaction decreasing noticeably as the shielding of the central atom increases.

The observation, made also by Launer,[5] that $MnC_2O_4^+$ undergoes decomposition more readily than does $Mn(C_2O_4)_2^-$ can be understood in the following way. The activated state for the separation of $MnC_2O_4^+$ into $Mn^{++} + C_2O_4^-$ (or $Mn^+ + 2CO_2$) will already partake largely of the properties of the products. The ion $MnC_2O_4^+$ is known to interact strongly with $C_2O_4^=$, but no evidence exists for an equally strong interaction of Mn^{++}. The effect of adding a second oxalate radical will therefore be to stabilize the initial state relative to the activated state, and thus lead to a high activation energy for the decomposition of $Mn(C_2O_4)_2^-$ as compared to $MnC_2O_4^+$. A small contribution to the reaction by direct decomposition of $Mn(C_2O_4)_2^-$ is not excluded by the considerations above nor by the data, and in fact a reaction of this type is suggested by the results of Bradley and Van Praagh.[15] On the basis of present results the specific rate of the change involving direct decomposition of $Mn(C_2O_4)_2^-$ must however be very much less than that for the decomposition of $MnC_2O_4^+$. The observed decrease in the rate of reaction of Mn(III) with the reducing intermediate as the number of associated oxalates increases can be interpreted by considerations similar to those presented above.

A correlation of the present work with that of Launer[5] is possible by calculating from his data the value for the equilibrium quotient: $(MnC_2O_4^+)(C_2O_4^=)/(MnC_2O_4)_2^-$ and comparing it with that obtained from the present work. The equilibrium concentrations of $C_2O_4^=$ and $Mn(C_2O_4)_2^-$ in his experiments can be estimated from his data, and the concentration of $MnC_2O_4^+$ can be calculated by comparing the specific rate for reaction 1 obtained in the present work with his observed rate of reaction. When this is done for the data of experiment 2, described in Fig. 2 of his paper (ref. 5), the quotient above is calculated to be 3×10^{-5}. The present work gives a value of about 10^{-7}. The discrepancy seems outside any that could be produced by ionic strength effects, and has as yet not been explained. If the quotient above is calculated in a similar way from the data of Bradley and Van Praagh (ref. 15, p. 1626, experiments 299–300) a value of about 10^{-7} at 16° is obtained. While this check as to order of magnitude with the value from the present work is satisfying, it cannot form the basis for definite conclusions since the ionic strengths and temperatures differ for the two sets of experiments. A value of 10^{-7} for the quotient under consideration however seems reasonable in a comparison with the value of 3.8×10^{-3} measured by Cartledge and Ericks[9] for the equilibrium between the dioxalato and trioxalato ions at 0°.

Summary

The rate of the reaction of chlorine and oxalic acid in the presence of trivalent manganese as catalyst has been studied as a function of the temperature and of the concentration of the various substances which influence the rate, and a rate law describing the data has been developed.

The initial rate of reaction is independent of the concentration of chlorine, is first order with respect to catalyst concentration and varies in a complex manner with the concentration of oxalic acid. The rate of the reaction, and the concentration of catalyst decrease with time of reaction.

The data are consistent with the following conclusions about equilibrium and rate processes which operate in the system.

The slow step in the catalysis is a unimolecular decomposition of the complex $MnC_2O_4^+$. The specific rate of this reaction at 25.2° is 11.4 ± 1 min.$^{-1}$, its activation energy is 18,300 ± 500 cal., and the frequency factor is 2×10^{14} min.$^{-1}$.

At low oxalic acid concentration the rate is decreased because the complex $MnC_2O_4^+$ is appreciably dissociated into a chloro-mangani complex ion and oxalic acid. The association constant for this equilibrium in 2 *M* hydrochloric acid at 25.2° is 5.1×10^3 and the association reaction is an endothermic process. At high oxalic acid concentration, the rate is decreased by the transformation of $MnC_2O_4^+$ to $Mn(C_2O_4)_2^-$. The equilibrium quotient for this association reaction in 2 *M* hydrochloric acid at 25.2° is 44 and this change is exothermic.

The catalyst Mn(III) is regenerated by a series of reactions involving the action of a reducing intermediate (which may be CO_2^-, $C_2O_4^-$ or Mn^+)

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(15) Bradley and Van Praagh, *J. Chem. Soc.*, 1624 (1938). The presentation of the interesting results obtained by these authors is somewhat marred by their assumption that sulfuric acid is completely dissociated under the conditions of their experiments. Recalculation on a correct basis may affect some of their conclusions.

formed by decomposition of $MnC_2O_4^+$, on chlorine to form atomic chlorine, and the oxidation of manganous ion to Mn(III) by atomic chlorine.

The catalyst undergoes net reduction by reaction with the reducing intermediate; the reducing intermediate reacts also with ferric ion. The specific rates of reaction of the reducing intermediate with chlorine, Mn_{Cl}^{+++}, $MnC_2O_4^+$, Fe(III) and $Mn(C_2O_4)_2^-$ decrease in that order.

CHICAGO, ILLINOIS RECEIVED MAY 15, 1946

[CONTRIBUTION FROM THE GEORGE HERBERT JONES AND KENT CHEMICAL LABORATORIES OF THE UNIVERSITY OF CHICAGO]

A General Theory of the Mechanism of Emulsion Polymerization[1]

BY WILLIAM D. HARKINS

I. Early Development

The general theory of the mechanism of emulsion polymerization presented here had its origin in ideas developed while the writer was a consultant for the Research Laboratory of the United States Rubber Company at Passaic, New Jersey, and later in work begun on December 15, 1942, for the Rubber Director's Office. In the beginning the consideration of this problem was undertaken at the suggestion of E. Hazell, manager of the Passaic Laboratory, who pointed out that at that time nothing was known as to the loci in which emulsion polymerization occurs. The general features of the theory were presented in a report of the writer (March 20, 1943). In this report data were presented on the increase of polymer particle size with increase in the yield of polymer. It was pointed out that these data were obtained by a soap titration method developed by H. F. Jordan (in 1931) for the determination of the area of carbon blacks.

At the suggestion of Dr. Jordan, this method had been applied by R. H. Ewart and L. M. White[1a] to the determination of particle size in GR-S latex.

The following statements were reported: (1) agreement between soap titration and ultracentrifugal measurements made at the University of Wisconsin; (2) increasing the soap concentration or temperature of polymerization decreases the particle size; (3) increasing the yield increases the particle size; (4) increasing the OEI has very little effect on the size.

By an application of the soap titration method it was found that soap disappears rapidly from the latex as the yield of polymer increases. These facts suggested to the writer that an early locus of polymerization is in the soap micelles and that this is shifted to the polymer particles as the yield increases. One of the reports issued by United States Rubber in March, 1942, showed that styrene vapor, when passed into water which contains potassium persulfate, polymerizes readily. This shows that soap is not essential if only a very slow polymerization is desired.

Extensive evidence for the theory has been obtained by M. L. Corrin, R. W. Mattoon and R. S. Stearns, who have continued their work since early in 1943, with Stearns and Corrin engaged in the physico-chemical aspects of the problem and Mattoon engaged in the X-ray work. The other co-workers are cited later in connection with their specific researches; Reynolds and his co-workers at the University of Cincinnati were associated with the writer in the early development of the project and did valuable work at that time, especially on solubilization, rate of polymerization, and the effects of salts. Simultaneously and even earlier, work on solubilization was carried out by Professor McBain at Stanford University.

One of the topics investigated in the earliest work at the University of Chicago was the effects of "seeding" or inoculation of a latex with latex formed in another system. It was found that the induction period, often four hours in length, caused by atmospheric oxygen in the polymerization of styrene, could be reduced or removed by the initial addition of latex in which some degree of polymerization had already been attained. This was suggested to McBain as a profitable subject for investigation and he, after the completion of experimental work in this field, considered it to give evidence in favor of the general theory of the writer. Whereas a modification of the "seeding" technique may be made to give powerful evidence for the theory, ordinary seeding itself, as practiced in the early work, seems to speak neither for nor against the theory.

Much encouragement in the researches carried out by the writer and his associates was given by W. A. Gibbons, of the United States Rubber Company, and by the chiefs of the Polymer Research Branch of the Rubber Director's Office and the Rubber Reserve Company: R. R. Williams, Calvin Fuller, R. F. Dunbrook and W. A. Borders.

Although the ideas presented in the paper are believed to be those of the author, he would like to point out that, during the past four years, he has attended numerous research discussion meet-

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(1) This investigation was carried out under the sponsorship of the Reconstruction Finance Corporation, Office of Rubber Reserve, in connection with the Government's synthetic rubber program.

(1a) R. H. Ewart and L. M. White, private communications, October 28 and November 5, 1941.