[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE THERMAL REACTION BETWEEN POTASSIUM OXALATE AND MERCURIC CHLORIDE

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The oxidation of oxalates by mercuric chloride as expressed by the following equation

$$2HgCl_2 + C_2O_4^{--} = Hg_2Cl_2 + 2Cl^- + 2CO_2$$

has been studied by a large number of investigators during the past seventy-five years. It is not surprising that the conclusions drawn by the various investigators should be lacking in agreement, since the reaction is influenced by both positive and negative catalysts. The reaction is sensitive not only to heat, but also to light of a frequency range extending all the way from the visible to the very hard x-rays. The present investigation, which deals with the thermal reaction in neutral aqueous solutions, is the first section of a more general investigation of this reaction.

Methods of Measuring the Rates of Reaction.—Two methods were used for making the kinetic measurements. The first consisted in sealing the reacting solutions in pyrex flasks, which were kept in a thermostat at the desired temperature for definite lengths of time, after which they were removed from the thermostat and quickly plunged into cold water. The bulbs were broken open and the amount of mercurous chloride formed was determined gravimetrically. In some cases, however, the amount of mercury remaining in solution was determined by precipitating as sulfide.

A second method was used where samples for analysis were drawn at different times from the same solution. This method involved the use of the apparatus shown in Fig. 1, which consists of a one and one-half liter pyrex bulb with a 1-mm. capillary sealed in through the top and extending to 0.5 cm. from the bottom. A is an all-glass condenser about 12 cm. long, through which the capillary passes to the capillary stopcock. Inside the condenser the capillary is thin walled to facilitate the rapid cooling of the contents while a sample is being taken. The tube B was used to introduce the reaction mixture, after which it was sealed off at the constriction. The bulb was immersed in a thermostat up to the point C. Water was passed through the condenser jacket and through a coil of copper tubing which was placed around the stopcock to keep the stopcock grease from melting and blowing out, but which could be removed when a sample was to be withdrawn. The vapor pressure of the water and carbon dioxide in the bulb gave a total pressure of about two atmospheres, which forced the solution out through the capillary when the stopcock was opened.

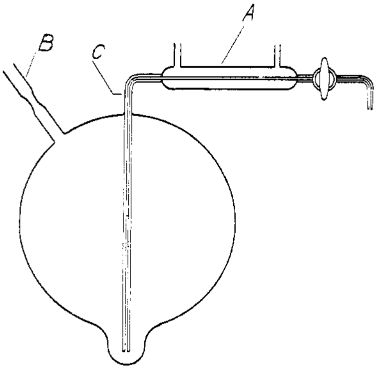

Fig. 1.

Before taking a sample, sufficient solution was run out to wash out the capillary and then the sample was taken in a test-tube, which was cooled to room temperature in a water-bath. A five or ten-cc. portion was measured out with a pipet, filtered free of mercurous chloride and acidified with hydrochloric acid to prevent any further reaction. The solutions were analyzed for mercury by precipitating with hydrogen sulfide and weighing as sulfide. The reaction vessels were always cleaned with hot chromic acid which was followed by hot concentrated hydrochloric acid to insure the removal of traces of iron. It was found that the results were more reproducible when the hydrochloric acid was used. The potassium oxalate, potassium chloride and mercuric chloride used were all twice recrystallized from the C. P. materials, whose analyses were given as containing 0.001% iron. The solutions were made up with ordinary distilled water.

The "zero" of time, in this method of measuring the rate, was not taken as the time when the apparatus was placed in the thermostat, but was taken as the time when the first sample was withdrawn, which was about half an hour after placing it in the thermostat. In this way the effect of the lag in coming to the temperature of the thermostat was avoided. Measurements by both methods were carried out in a paraffin thermostat regulated to within 0.1° at 100° and 0.15° at 120°. The solutions were mixed and analyzed in dim artificial light but at other times were kept in the dark.

The Reaction in the Absence of Oxygen.—The reaction is sensitive to very small traces of oxygen and so it was necessary to use great care to insure its removal. The oxygen was removed by saturating the solutions with pure carbon dioxide at atmospheric pressure and then the carbon dioxide was boiled out of the solutions under reduced pressure, carrying the oxygen with it. This process was repeated six times, giving solutions with much less oxygen than could be obtained by passing oxygen-free carbon dioxide through the solutions for six hours. The bulbs were then filled with purified carbon dioxide to atmospheric pressure at 25° and sealed off. The carbon dioxide was freed from oxygen by passing it through copper turnings heated to 400°. In spite of these precautions, there appeared to be sufficient oxygen left to affect the rate. This was the principal cause of the difficulty in obtaining reproducible results.

The Effect of the Mercuric Chloride.—The order of the reaction with respect to mercuric chloride was determined by using a solution where the amount of potassium oxalate was equivalent to about ten times the quantity of mercuric chloride present. Under these conditions the total observed order of the reaction would be that of the mercuric chloride. Table I shows the results of such an experiment made by the second method where samples were drawn from the same solution.

TABLE I

100°; ATM. PRESSURE OF CO_2; KCl, 0.0909 *M;* $K_2C_2O_4$, 0.405 *M;* $HgCl_2$, 0.0836 *M*

Minutes	0	65	143	262	428	549	
HgS (5 cc.)	0.0819	0.0751	0.0672	0.0567	0.0466	0.0374	
−Log HgS	1.087	1.124	1.173	1.246	1.351	1.427	
K (1st order) × 10^5		57	60.2	60.7	61.7	61.9	Mean, 61

This shows that the velocity of the reaction is very nearly proportional to the first power of the total mercury in solution. No correction was made for the retarding effect of chloride ion formed in the reaction. If such a correction were made it would give an upward trend to the constants, making it appear less than first order. Such a trend may be explained as due to the increased dissociation of Hg_2Cl_4[1] which would occur when the $HgCl_2$ is used up in the reaction.

The Effect of Chloride Ion.—When chloride ion is added to the solution the rate of reaction is decreased. Tables II and III give results when the chloride-ion concentration is large compared to the concentration of the mercuric chloride. The two parts of each table represent duplicate experiments using the large bulb.

TABLE II

100°; ATM. PRESSURE OF CO_2; KCl, 0.3636 *M*; $K_2C_2O_4$, 0.405 *M*; $HgCl_2$, 0.0836 *M*

Minutes	HgS (10 cc.)	−Log HgS	*K* (1st order)
0	0.1863	0.7298	
507	.1399	.8542	24.5×10^{-5}
979	.1105	.9566	23.2×10^{-5}
2077	.0735	1.1337	19.5×10^{-5}
0	.1915	0.7178	
507	.1381	.8598	28.0×10^{-5}
979	.1050	.9788	26.7×10^{-5}
2077	.0673	1.1720	21.9×10^{-5}
			Mean, 24.1×10^{-5}

TABLE III

SAME AS TABLE II EXCEPT KCl, 0.7272 *M*

Minutes	0	346	1030	1752	0	1030	2595	
HgS	0.1929	0.1816	0.1662	0.1535	0.1910	0.1659	0.1447	
−Log HgS	0.7147	0.7409	0.7794	0.8139	0.7190	0.7801	0.8395	
K (1st order) $\times 10^5$	....	7.6	6.3	5.7	....	5.9	4.6	Mean, 6

It will be observed that the mean rate in Table II is almost exactly four times that in Table III. Since the chloride ion is in large excess and the concentration is doubled in the latter, it is evident that the rate varies as the inverse second power of the chloride-ion concentration when the latter is large. The mercury, under these conditions, is nearly all present as $HgCl_4^{--}$ as shown by the equilibrium $(HgCl_2) = k(HgCl_4^{--})/(Cl^-)_2$. Therefore, the rate is proportional to the concentration of the $HgCl_2$ molecules under all conditions, the chloride-ion concentration only affecting the concentration of the $HgCl_2$.

There is a marked downward trend in Tables II and III which can be accounted for by the retarding action of the chloride ion formed during the reaction. The retarding effect of the chloride ion formed during the reaction is greater, the larger the initial chloride-ion concentration. This

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[1] G. A. Linhart, THIS JOURNAL, **37**, 271 (1915).

is because there are, for each atom of mercury reduced, three times as many chloride ions formed when the chloride-ion concentration is large as when it is small. The main reaction for very large and very small ion concentrations may be represented as $HgCl_4^{--} + (-) = {}^1/_2Hg_2Cl_2 + 3Cl^-$ and $HgCl_2 + (-) = {}^1/_2Hg_2Cl_2 + Cl^-$. We do not know the dissociation constant of $HgCl_4^{--}$ at 100°; therefore we cannot make an accurate correction for the retarding effect of the chloride ion formed. However, a calculation was made assuming a negligible dissociation and this fully accounted for the trend in Table II and for half the trend in Table III.

The Effect of the Oxalate.—The effect of the oxalate concentration was determined using an excess of oxalate with a solution similar in every respect to the solution in Table I except that the oxalate concentration was made exactly one-half as large. The results for this solution listed in Table IV give a mean of 14×10^{-5}. The mean of Table I is 61×10^{-5}.

TABLE IV

AT 100°; ATM. PRESSURE OF CO_2; KCl, 0.0909 *M*; $K_2C_2O_4$, 0.2025 *M*; $HgCl_2$, 0.0836 *M*

Minutes	0	118	353	702	1293	
HgS	0.0924	0.0893	0.0831	0.0754	0.0574	
−Log HgS	1.034	1.049	1.080	1.123	1.241	
K (1st order) $\times 10^5$	....	13	13	13	16	Mean, 14

This value is equal to four times the mean value in Table IV. Since the oxalate concentration in Table I is twice that of the oxalate in Table IV, the rate varies as the second power of the oxalate concentration.

The power of the oxalate in the kinetic equation was also determined under conditions where the mercuric chloride was in excess, by the method of sealed bulbs. In this case the total observed order of the reaction will be that of the oxalate since there will be only a negligible change in the mercury concentration.

TABLE V

120°; CO_2 PUMPED OFF BEFORE SEALING; KCl, 0.05 *M*; $K_2C_2O_4$, 0.0100 *M*; $HgCl_2$, 0.0989 *M*

Minutes	0	780	1481	3856
Hg_2Cl_2	.....	0.0323	0.0517	0.0773
$(a - x)$	0.00100	0.00726	0.00558	0.00345
$1/(a - x)$	100	138	179	290
K (2d order)	.....	0.049	0.053	0.050

TABLE VI

120°; CO_2 PUMPED OFF BEFORE SEALING; $HgCl_2$, 0.0989 *M*; $K_2C_2O_4$, 0.00997 *M*

Minutes	0	405	606	2140
Hg_2Cl_2	.....	0.0396	0.0493	0.0855
$(a - x)$ mole/liter	0.00997	0.00664	0.00576	0.002758
$1/(a - x)$	100.3	150.6	173.6	363.0
K (2d order)	.....	0.124	0.121	0.123

These results are given in Tables V and VI. Potassium chloride was added to the former but not to the latter. In both cases, however, the rate obeys a second-order law, showing that the rate is proportional to the second power of the oxalate concentration when the mercuric chloride is large as well as when the oxalate is in excess.

The Reaction in the Presence of Oxygen.—Oxygen not only retards the reaction but changes the order of the reaction with respect to the oxalate. This change depends on the pressure of oxygen and upon the concentration of the reactants. It was necessary to measure the rates in short enough time intervals so that we could neglect the change of concentration of the reaction materials. In Table VII the quantity of oxygen is stated in terms of millimoles of oxygen admitted to the flasks.

Table VII

100°; $K_2C_2O_4$, 0.200 *M;* $HgCl_2$, 0.12 *M;* KCl, 0.100 *M*

Oxygen	0.223	0.446	0.892	1.784	3.568
Minutes	60	60	255	255	255
Hg_2Cl_2, g.	0.1318	0.0798	0.1516	0.1085	0.0847
Rate, Hg_2Cl_2/min.	0.00220	0.00133	0.00059	0.00043	0.00033
Rate, calcd.	0.00222	0.00120	0.00069	0.00043	0.00031

The concentration of oxygen in solution would be proportional to this quantity, since the volume of each flask was 152 cc. After 50 cc. of the solution was placed in each flask the air was pumped out and the stated amount of oxygen admitted before sealing off. For the lower concentrations of oxygen the rate is nearly inversely proportional to the oxygen concentration, but at higher concentrations of oxygen its effect is much less. Analyses of the gas remaining in the flasks as well as of the resulting solutions showed that the oxygen did not oxidize determinable amounts of the oxalate.

The rate here may be best expressed by the equation

$$\frac{dx}{dt} = \frac{1}{k'\,(O_2)} + k'' \qquad (1)$$

If k' is assumed to be 22×10^2 and k'' to be 18×10^{-5}, one obtains the calculated values of the rate given in the last column of Table VII. In Fig. 2 the experimental rates are given by the circles while the calculated values fall identically on the curve. This shows that the calculated values obtained from the above equation lie on the best smooth curve drawn through the experimental points.

The Effect of the Mercuric Chloride with Oxygen Present.—The order of the reaction was determined using an excess of oxalate so that the total observed order was that of the mercuric chloride.

The results obtained by the method of small flasks are given in Table VIII, which shows that the rate of the reaction is proportional to the first power of the concentration of the mercuric chloride. The retarding effect

TABLE VIII

100°; ATM. PRESSURE OF O_2 WHEN AT 25°; TRACE OF CO_2; $K_2C_2O_4$, 1.796 *M;* $HgCl_2$ 0.0968 *M*

Minutes	0	206	450	974	1464	1890
HgS	0.2255	0.1794	0.1414	0.0904	0.0554	0.0394
−Log HgS	0.6468	0.7462	0.8495	1.0438	1.2565	1.4045
K (1st order) × 10^5		48	45	41	42	40

of the chloride ion formed in the reaction is sufficient to account for the downward trend in the rate constants. With oxygen present it is impossible to determine the effect of chloride ion when the latter is in excess, since then the reaction is immeasurably slow.

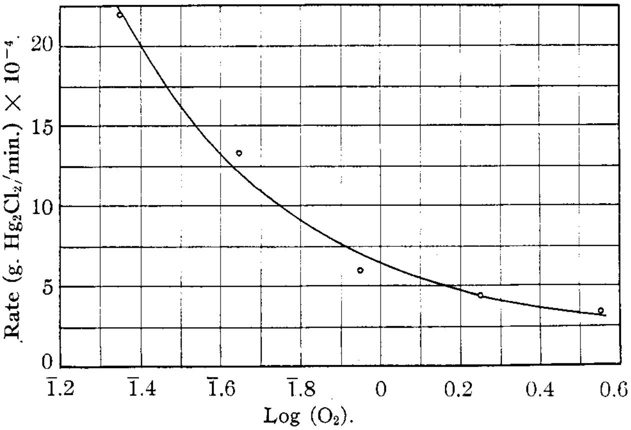

Fig. 2.

The Effect of the Oxalate with Oxygen Present.—The order of the reaction with respect to the oxalate was determined by using a solution similar to that in Table VIII in every way except that the concentration of the oxalate was one-half as great.

TABLE IX

SAME AS TABLE VIII EXCEPT $K_2C_2O_4$, 0.898 *M*

Minutes	0	1149	1460	2997
HgS	0.2255	0.1155	0.0985	0.0533
−Log HgS	0.6468	0.9374	1.0066	1.2733
K (1st order) × 10^5	....	25.3	24.6	20.9

The results given in Table IX show a rate that is one-half the rate in Table VIII; therefore the rate is proportional to the first power of the concentration of the oxalate.

The Effect of Iron Salts.—The effect of oxygen depends on the amount of iron salts present in the solution. The addition of one part of ferrous salt to 100,000 parts of mercuric chloride will change the order of the reaction with respect to the oxalate from second to first when an appropriate concentration of oxygen is present. This accounts for the results of Dahr,[2] who found that the rate varied as the first power of the oxalate concentration in solutions made from C. P. materials when saturated with carbon dioxide. Table X shows that the reaction is first order with respect to the oxalate when a small amount of iron salt is added, even when the pressure of the oxygen was too small to measure with an ordinary manometer.

TABLE X

120°; TRACE OF O_2; $HgCl_2$, 0.100 *M;* $K_2C_2O_4$, 0.0100 *M;* $FeCl_3$, 0.004 *M*

Minutes	0	360	653	1448
Hg_2Cl_2	....	0.0363	0.0583	0.0900
$(a - x)$, mole/liter	0.0100	0.00693	0.00506	0.00238
$-\text{Log}\ (a - x)$	2.000	2.159	2.296	2.623
K (1st order) $\times 10^5$	....	44	45	43

Ordinary C. P. mercuric chloride and potassium oxalate, in which the analysis as stated on the container admitted 0.001% iron, also were found to give a rate proportional to the first power of the oxalate concentration. This appears to be due to the iron salts contained in them since the recrystallized chemicals react with a rate proportional to the second power of the oxalate concentration under the same conditions.

Discussion and Summary

The experimental results may be summarized by the equation

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{k_1(\mathrm{HgCl_2})(\mathrm{C_2O_4}^{--})^2}{k_2(\mathrm{O_2}) + k_3} + \frac{k_4(\mathrm{HgCl_2})(\mathrm{C_2O_4}^{--})(\mathrm{Fe}^{++})^x(\mathrm{O_2})^z}{k_5(\mathrm{O_2})^z + k_6}$$

k_3 is necessary in order that the rate does not approach infinity as the concentration of oxygen is continually decreased. It is so small, however, that it could be neglected in all experiments where oxygen was admitted. Under all conditions the rate is proportional to the concentration of the $HgCl_2$ molecules. Chloride ion does not occur in the equation since it changes only the concentration of the $HgCl_2$ by forming $HgCl_4^{--}$. When the concentration either of oxygen or ferrous ion is large the first term can be neglected and the rate will be proportional to the first power of the oxalate concentration. On the other hand, when the concentration of the oxygen is very small, the first term is large and the second term can be neglected, making the rate proportional to the second power of the oxalate concentration. When the concentration of the mercuric chloride, oxalate and ferrous ion is constant the rate will be given by

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{1}{k_2'(\mathrm{O_2}) + k_3'} + \frac{k_4'(\mathrm{O_2})^z}{k_5(\mathrm{O_2})^z + k_6}$$

However, k_3 and k_6 are so small that they may be neglected in all the experiments where oxygen was present. Then the equation reduces to

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{1}{k_2'(\mathrm{O_2})} + k_4''$$

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[2] N. R. Dahr, *J. Chem. Soc.*, **111**, p. 752 (1917).

which was found to be true experimentally. The presence of two terms in the kinetic equation indicates that there are two reactions proceeding simultaneously, the total rate being the sum of the two separate rates. Winther[3] studied the effect of ferrous salts on the reduction of mercuric chloride by ammonium oxalate in the presence of oxygen at room temperature. He found that the oxidation of ferrous oxalate by oxygen induced the reaction to take place, giving as many as 4000 molecules of mercurous chloride per molecule of ferrous oxalate oxidized by oxygen, but this number decreased with increasing oxygen concentration. However, there was no reaction when oxygen was absent. It is evident that the reaction observed by Winther must take place at 100° when oxygen and iron are present, even though in very small amounts. In the present investigation it was found that ferric oxalate decomposes into ferrous oxalate and carbon dioxide at 100° at a moderate rate, so that there will be repeated oxidation of the ferrous iron by oxygen and reduction of ferric iron by oxalate. The first part of each cycle would cause a chain of some 4000 molecules of mercuric chloride to react with oxalate. The repetition of this cycle would account for the catalytic effect of such small quantities of iron. The quantity of oxygen consumed would be equivalent to less than one-thousandth of the oxalate or mercuric chloride reacting, which agrees with the experimental fact that practically no oxygen was used up in the reaction. The effect of iron is too complex to be expressed analytically at the present time as the fraction of the iron present in the ferrous form depends on the concentrations of oxygen and oxalate in the solution, even when one assumes that the steady state is quickly attained.

In the investigation of the photochemical reaction now in progress, the quantum efficiency has been found to be 3000 molecules reacting per quantum of light absorbed. It also is inhibited by oxygen. Dahr[4] has found that the reaction is induced by many oxidizing agents in the dark, giving as many as several thousand molecules of mercurous chloride per molecule of inductor transformed.

The effect of oxygen, therefore, must be three-fold: (a) the inhibiting effect in the first term as shown by the equation, (b) the oxidation of ferrous oxalate to ferric oxalate, thus increasing the number of chains in the second term, and (c) the shortening of the average length of the chain in the second term corresponding to a similar effect in the first term. From these considerations and the fact that the rate becomes independent of the oxygen concentration as the later is increased (see Equation 1), it seems evident that oxygen must occur in both numerator and denominator of the second term to the same power. At the low concentrations of oxygen which would be necessary to determine k_6, the value of the first term

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[3] Chr. Winther, *Z. Wiss. Phot.*, **7**, 411 (1908).

[4] N. R. Dahr, *Ann. chim.*, **11**, 197 (1919).

of the rate equation is so great as to make such a determination impossible. On the other hand, if the concentration of the ferrous salt is made large, the retarding effect of the resulting ferric ion, which was observed by Winther, will be large in comparison to k_6. When the concentration of oxygen is large, k_6 and the first term of the equation may be neglected. Under these conditions the oxygen cancels out of the second term and the rate is independent of the oxygen concentrations.

The discussion of the mechanism of the chains occurring in these reactions will be postponed until more work has been done on the reaction in acid solution and on the photochemical reaction.

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THE CHEMICAL EFFECTS OF HIGH FREQUENCY SOUND WAVES
II. A STUDY OF EMULSIFYING ACTION

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One of the most spectacular manifestations of the effects of the high frequency sound waves produced by Wood and Loomis[1] is their emulsifying action on benzene, paraffin and even mercury in contact with water. Since this action promises to be of some practical value and since, moreover, it gives important indications of the nature of sound wave effects, it has been briefly investigated.

1. The Mutual Emulsification of Two Liquids.—When benzene and water are placed in a test-tube which has been previously wet with water and the tube is irradiated with intense sound waves of 300 K.C., the benzene layer at once becomes cloudy, the water layer more slowly so and, finally, the boundary between the two disappears. A similar action may be observed between water and any other liquid of similar physical properties; even medicinal paraffin follows the same course. With high intensities of sound the agitation of the interface is, however, so intense that reliable observation of the locality at which emulsification occurs is impossible.

In order to verify the suspicion that emulsifying action occurs primarily at the wall in contact with benzene and not at the liquid–liquid interface, very low intensities of sound (roughly one-tenth of those employed by Wood and Loomis, and the author and Loomis,[2] and designated by the latter 100%) were used, and the following results obtained.

In water-wet tubes containing a benzene–water interface the white

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[1] R. W. Wood and A. L. Loomis, *Phil. Mag.*, [vii] **4,** 417 (1927).

[2] W. T. Richards and A. L. Loomis, THIS JOURNAL, **49,** 3086 (1927).