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

THE X-RAY PHOTOCHEMICAL REACTION BETWEEN POTASSIUM OXALATE AND MERCURIC CHLORIDE

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Many investigators have studied the photochemical reaction between mercuric chloride and oxalates as represented by the equation

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

The results, however, have not been satisfactory due to three uncertainties, namely, the catalysis of very small traces of iron salts, the inhibition by oxygen and the formation of a white precipitate which reflects the light, making the amount of light absorbed by the solution uncertain. In the present investigation these uncertainties were eliminated.

Experimental

Apparatus.—The cylindrical reaction chamber A shown in Fig. 1 was made by fusing together the bottoms of two 250-cc. pyrex beakers. This was surrounded by a glass water jacket through which water from the thermostat was pumped. The front side was covered with a layer of cotton which provided thermal insulation yet only slightly absorbed x-rays. The length of the chamber was 6.8 cm. and the diameter 6.5 cm. The chamber was connected to the mercury manometer by a small glass capillary and a 15-cm. length of capillary rubber tubing B. The height of the mercury in the manometer was measured with the aid of a cathetometer to one-tenth of a millimeter. All measurements were made at constant volume with the mercury at the point C so that the volume of the tubing connected to the reaction chamber was relatively so small that a change of 10° in the temperature of the room would not change the pressure 0.05%. The reaction chamber was supported by a shaking mechanism which gave it short and sharp jerks, thereby shaking the solution vigorously.

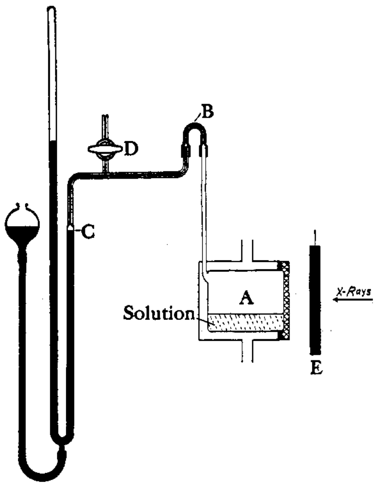

Fig. 1.

The x-rays were generated by a Coolidge x-ray tube operated directly on 60-cycle alternating current with a peak voltage of 120,000. The power input was kept constant by means of ballast tubes. The tungsten target was 50 cm. from the reaction vessel and the latter was entirely exposed to the rays when the shutter E was open.

The energy of the x-rays entering the reaction chamber was determined by the calorimeter shown in Fig. 2. The center part F is a lead disk 2.50 cm. in diameter and 0.85 mm. thick which is supported in the center of a heavy iron ring G by the forty wires of the chromel–x–copel thermopile. The flattened junctions of the thermopile were attached to the disk by means of a thin layer of sealing wax which provided both thermal contact and electrical insulation. A spiral coil made from 15 cm. of No. 40

silk-covered manganin wire was imbedded in a thin layer of sealing wax on the face of the lead disk. Two No. 36 copper wires led out from the coil making thermal but not electrical contact with the heavy iron ring before passing out of the case. The resistance of the manganin coil was 20.57 ohms. The iron ring was suspended by means of silk thread in a glass case with a thin aluminum window in front of the lead disk. This case was packed in cotton to prevent air currents and radiation in the room from affecting the thermopile. A lead screen H shielded the iron ring from the x-rays.

The mercuric chloride, potassium oxalate and potassium chloride were all twice recrystallized from the c. p. quality materials. The ferric chloride used was Baker's c. p. The carbon dioxide was obtained from a cylinder and passed over fresh copper turnings at 400° to remove oxygen.

Experimental Procedure.—In all cases 50 cc. of solution was measured into the reaction chamber with a pipet. The rubber capillary tube was then slipped over the neck, fastened with wire and then coated with paraffin to prevent any leaks. In order to remove the oxygen, which inhibits the reaction, the apparatus was evacuated to within 5 mm. of the vapor pressure of water and then oxygen-free carbon dioxide admitted to atmospheric pressure. The chamber was shaken vigorously for two minutes to saturate the solution with the carbon dioxide and to shake out the oxygen into the carbon dioxide above the solution. This same process of evacuating and admitting carbon dioxide was repeated nine times. The carbon dioxide would boil vigorously out of the solution for about two minutes under the reduced pressure, carrying the oxygen out with it. Before measuring the rate, the vacuum stopcock D was closed and the apparatus shaken until the pressure no longer changed. The manometer was read and then the lead x-ray shutter E was opened for a definite length of time. The chamber was again shaken until the pressure became constant and then the manometer was read.

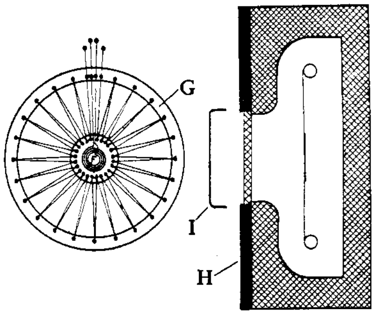

Fig. 2.

The energy of the x-rays was determined by placing the calorimeter in the exact position in which the center of the reaction chamber had been in all the experiments. The reaction chamber was broken in half and the front end placed in front of the calorimeter so that the latter would directly measure the power entering the reaction chamber in all experiments for the area of the lead disk. When the x-rays were turned on, the galvanometer connected to the thermopile gave a deflection of about 20 cm. The x-rays were shut off and a current was started through the manganin coil. This current was adjusted until the galvanometer gave the same deflection as with the x-rays. Then the power of the absorbed x-rays would be equal to I^2R where R is the resistance of the manganin coil and I the current passed through it. This current was repeatedly found to be 1.55 milliamperes.

Experimental Results

Effect of Mercuric Chloride Concentration.—The order of the reaction with respect to mercuric chloride was determined using a solution in which the amount of potassium oxalate was equivalent to more than 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. The results are given in Tables I and II, respectively, with and without the ad-

TABLE I

25°, $HgCl_2$ 0.1164 *M*, $K_2C_2O_4$ 0.620 *M*, OXYGEN FREE

Minutes	Pressure (CO_2 + H_2O)	$(a-x)$ mole/liter	$-\text{Log}\ (a-x)$	*K* (1st power)
0	2.74	0.1164	0.9342	...
1	8.49	.1005	0.9977	0.0635
2	13.22	.0865	1.0632	.0655
4	20.79	.0649	1.1879	.0624
6	26.02	.0450	1.3014	.0568
11	33.69	.0281	1.551	.050
25	41.09	.0070	2.126	.043
40	43.20	.0038	2.418	.018
0	3.04	.1164	0.9342	
1.5	11.60	.0919	1.0365	.0682
2	14.12	.0848	1.0718	.0706
3	18.37	.0726	1.1389	.0671

TABLE II

25°, $HgCl_2$ 0.1164 *M*, $K_2C_2O_4$ 0.620 *M*, KCl 0.2327 *M*

Minutes	Pressure, cm.	$(a-x)$ mole/liter	$-\text{Log}\ (a-x)$	*K* (1st Power)
0	2.65	0.1164	0.9342	...
1	4.64	.1107	0.9558	0.0216
3	8.49	.0998	1.0011	.0225
7	14.85	.0816	1.0883	.0218
11	19.52	.0683	1.1658	.0194
16	23.84	.0559	1.2522	.0173
25	29.16	.0408	1.3897	.0153
45	35.76	.0219	1.6588	.0135

dition of potassium chloride. The rate approximates a first-order law until the reaction is near completion and then the rate rapidly falls off. Such a decrease is to be expected due to the retarding effect of the chloride ion formed by the reaction. Also, as the reaction proceeds, a larger proportion of the energy will be absorbed by the mercurous chloride precipitate and this should cause a decrease in the observed reaction rate. In order to avoid these effects, the rate was measured using a solution similar to those of Table I except that the mercuric chloride concentration was made exactly one-half as large. The rate constant in Table III, is in good agreement with that in Table I, and therefore it is evident that the rate of the reaction varies as the first power of the mercuric chloride concentration. It will also be noted that in all cases the rate constant increased during

TABLE III

SAME AS TABLE I EXCEPT $HgCl_2$ 0.0582 *M*

Minutes	Pressure	$(a-x)$	$-\text{Log}\ (a-x)$	*K* (1st Power)
0	2.56	0.0582	1.2352	...
1.5	6.74	.0463	1.3348	0.0664
3.5	11.11	.0338	1.4713	.0687

the first part of the reaction, thus showing an induction period which is characteristic of many other chain reactions.

Effect of Oxalate Concentration.—The order of the reaction was determined for a solution containing equivalent amounts of oxalate and mercuric chloride. The results given in Table IV, show that the rate obeys a second-order law. Since the reaction is first order with respect to the mercuric chloride it seems evident, under these conditions, that the rate varies as the first power of the oxalate concentration. However, this is not true where the equivalent concentration of the oxalate is greater than the concentration of the mercuric chloride. The effect of the oxalate at various concentrations was determined using solutions similar in every way except having different oxalate concentrations and measuring the rate during a short interval of time during which there would only be a negligible change in the composition of the solution. These results are summarized in Table V. In the first two solutions, doubling the concentration of the oxalate almost exactly doubles the rate, but as the latter concentration is increased the effect of doubling it grows very small. Such a change in the effect of the oxalate suggests that the reaction is the decomposition of a moderately stable complex between mercuric chloride and the oxalate. The calculated values of the rate given in the table were obtained by assuming the rate equation $dx/dt = 0.575(HgCl_2C_2O_4^{=})$ and the equilibrium: $(HgCl_2)(C_2O_4^{=}) = 0.01\ (HgCl_2C_2O_4^{=})$. The agreement between the calculated and measured values of the rate, over a twenty-fold range of concentration, is strong evidence that the reaction is the decomposition of the

TABLE IV

$HgCl_2$ 0.116 *M*, $K_2C_2O_4$ 0.580 *M*

Minutes	Pressure	$(a-x)$ mole/liter	$\frac{1}{(a-x)}$	*K* (2nd Order)
0	2.56	0.1164	8.58	..
0.5	4.06	.1123	8.91	0.66
1	5.45	.1081	9.25	.68
2.5	9.08	.0978	10.23	.65
4	12.15	.0890	11.24	.67
7	17.31	.0742	13.46	.74
11	22.23	.0603	16.60	.78
16	26.06	.04934	20.27	.73
24	29.63	.03915	25.25	.62

TABLE V

25°, $HgCl_2$ 0.1164 *M*

$K_2C_2O_4$ concn.	0.0291	0.0582	0.155	0.310	0.620
Rate (meas.)	.0151	.0316	.0574	.0615	.066
Rate (calcd.)	.0151	.0290	.0568	.0638	.066
$(HgCl_2C_2O_4^{-})$	.0262	.0505	.0988	.111	.114

complex $HgCl_2C_2O_4^{=}$. Bekhterev[1] has shown that mercuric chloride forms a complex with potassium oxalate.

Effect of Chloride Ion.—Chloride ion retards the reaction at all concentrations, but the extent varies with the concentration. This effect was investigated by measuring the rates of reaction of solutions differing only in the chloride-ion concentration. The rates were measured during short intervals of time so that there would only be a negligible change in the concentrations. The results are given in Table VI. At higher concentrations of chloride ion, doubling the concentration makes the rate one-quarter as large, so that the rate varies as the inverse second power of the chloride-ion concentration. At lower concentrations, however, the effect becomes less. This is what one would expect from the equilibria $(HgCl_2)(Cl^-) = k(HgCl_3^-)$ and $(HgCl_2)(Cl^-)^2 = k' (HgCl_4^{=})$. When the chloride-ion concentration is large, the mercury will nearly all be present as $HgCl_4^{=}$ and then the concentration of the $HgCl_2$ would be inversely proportional to the second power of the chloride-ion concentration. Therefore, the rate must be proportional to the concentration of the $HgCl_2$ molecules.

TABLE VI

25°, $HgCl_2$ 0.1164 *M*, $K_2C_2O_4$ 0.620 *M*

KCl mole/liter	1.8616	0.9308	0.2327	0.1164	0.0000
Rate	0.00028	.00122	.0218	.0378	.066

The Effect of Oxygen.—Oxygen was found to inhibit the reaction at all observed pressures from 0.019 to 8.0 cm., a four hundred-fold range. The solutions were freed of oxygen and the given pressure of oxygen admitted, except for pressures below 0.4 cm., which were obtained by admitting known volumes of carbon dioxide containing 5% of oxygen. The rates were measured during short intervals of time during which the concentration did not change more than 2%. The results are given in Table VII. The calculated values of the rate given in the third column were obtained from the empirical equation

$$\frac{dx}{dt} = \frac{0.560}{0.0823 + (O_2)}$$

At the higher oxygen concentrations the rate is inversely proportional to the oxygen concentration, but at lower concentrations the effect of oxygen becomes less.

The Effect of Ferric Chloride.—The inhibition by ferric chloride was investigated in the same manner as the inhibition by oxygen. It was found impossible to obtain reproducible rate measurements with ferric chloride concentrations between 7 × 10^{-6} and 2 × 10^{-7}*M*. There is more uncertainty with the smallest iron salt concentration since under these conditions a trace of oxygen would induce an appreciable dark reaction at

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[1] Bekhterev, *J. Russ. Phys.-Chem. Soc.*, **57**, 161 (1925).

TABLE VII

25°, $HgCl_2$ 0.0972 *M*, $K_2C_2O_4$ 0.898 *M*

Oxygen press., cm.	Rate, %/min.	Rate (calcd.)
0.0000	6.8	6.8
.0192	6.18	5.5
.0383	4.73	4.6
.075	3.46	3.56
.148	2.52	2.43
.284	1.52	1.53
.40	1.14	1.16
.55	0.87	0.89
.86	.59	.59
1.89	.274	.284
4.03	.140	.136
8.05	.075	.069

TABLE VIII

25°, $HgCl_2$ 0.0972 *M*, $K_2C_2O_4$ 0.898 *M*, OXYGEN FREE

$FeCl_3$, $m \times 10^3$	Rate, %/min.	Rate (calcd.)
	6.8	
None	6.8	6.8
	6.9	
	3.77	
0.0078	3.82	3.95
	3.94	
.016	2.43	2.74
.062	1.08	1.01
.25	0.333	.29
	.336	
.50	.196	.14
1.00	.091	.073
	.095	

room temperature. Some of the results given in Table VIII are given in duplicate or triplicate to show their reproducibility. The values given in the third column of Table VIII were calculated from the empirical equation

$$\frac{dx}{dt} = \frac{0.560}{0.0823 + 7630(FeCl_3)}$$

This equation differs from that for oxygen only in that the (O_2) of the former is replaced by 7630 $(FeCl_3)$.

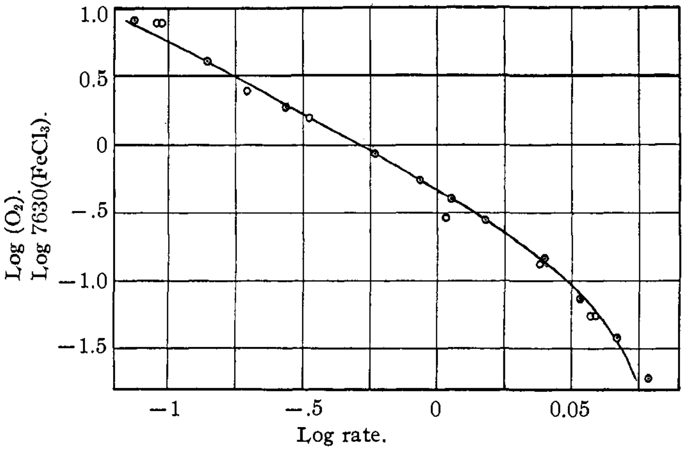

Fig. 3.

In Fig. 3 the logarithms of the rates are plotted against the logarithms of the oxygen pressures and also against the logarithms of 7630 times the ferric chloride concentrations. The curve represents both empirical equations, while the circles are the measured values with ferric chloride and the dot-centered circles are the measured values with oxygen. This graph shows that the empirical equations are in agreement with the experimental measurements.

There is no measurable dark reaction at room temperature unless both iron salts and oxygen are present at the same time, and this was not the case in any of the above experiments.

Temperature Coefficient.—The same solution was used for measuring the rate at both temperatures. Two thermostats, one at 25 and the other at 35° were arranged so that water from either could be circulated through the water jacket of the reaction chamber. The rate was measured at 25, then at 35 and then again at 25°. The manometer was always read with the solution at 25° to avoid any effect of the change of solubility of carbon dioxide with temperature. Five minutes were allowed for the temperature of the solution to come to that of the thermostat, both before reading the manometer and before turning on the x-rays. The solutions used were 0.1164 M $HgCl_2$, 0.290 M $K_2C_2O_4$, 0.2327 M KCl, all free from oxygen. Two separate measurements gave the temperature coefficient as 1.54 and 1.51 for ten degrees.

Energy Efficiency and Chain Length.—The power absorbed by the calorimeter was I^2R or $0.00155^2 \times 20.6$. This is 4.94×10^{-5} watt or 0.00071 cal./min. Since the reaction vessel containing 50 cc. of solution was 6.8 cm. long, the cross section of the solution would be 7.35 sq. cm. The area of the lead disk was 4.91 cm.^{2} and therefore the cross section of the solution was 1.50 times the area of the lead disk, so that the power entering the solution was 0.00106 cal./min. In Table I, the amount reacting during the first minute was 0.0008 mole. This gives the energy efficiency as 1.32 cal./mole or in other units 0.91×10^{-16} ergs per molecule. Since it takes 35 volts or 56×10^{-12} ergs on the average to produce an ion pair, there were 6×10^5 molecules reacting per ion pair. It is assumed that the total energy absorbed goes into ionization.

Summary and Conclusions

The rate of the reaction under all conditions studied is given by the following equation

$$\frac{dx}{dt} = \frac{k(HgCl_2C_2O_4^{=})}{0.0823 + (O_2) + 7630(FeCl_3)}$$

where $HgCl_2C_2O_4^{=} = 0.01\,(HgCl_2)(C_2O_4^{=})$. This is for constant energy input. The oxygen concentration is in centimeters pressure, while the other concentrations are in moles per liter. In all cases studied the incident radiation was constant and totally absorbed. This equation expresses the rate only when oxygen and ferric chloride are not both present at the same time. In that case, there is also an induced dark reaction[2] which must be added to this.

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[2] W. E. Roseveare and A. R. Olson, THIS JOURNAL, **51**, 1717 (1929).

The great energy efficiency indicates that it is a chain reaction. The denominators of the above equations are similar to those found by Bäckström[3] to express the negative catalysis of alcohols in the oxidation of sodium sulfite which is a chain reaction. The effect of oxygen and ferric chloride can best be explained by Bäckström's theory that the effect of the negative catalyst is to break the chains.

It seems probable that the primary step is the decomposition of the complex according to this equation

$$HgCl_2C_2O_4^{=} + \text{energy} = HgCl + Cl^- + C_2O_4^-$$

The half-oxidized oxalate, $C_2O_4^-$, would then reduce the $HgCl_4$ in another $HgCl_2C_2O_4^{=}$ and the energy of reaction may cause the oxalate ion in the complex to decompose, giving products which may react in the same way as the half-oxidized oxalate. These chains would end if the intermediate products were oxidized by either oxygen or ferric chloride. Such a mechanism is in agreement with the above experimental equation for the rate of reaction.

The observed temperature coefficient will be the sum of the temperature coefficients for the reaction and for the dissociation of the complex ions.

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A METHOD FOR DETERMINING THE VISCOSITY OF CORROSIVE GASES AND THE MOLECULAR DIAMETER OF NITROGEN PENTOXIDE

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Introduction

The decomposition of nitrogen pentoxide has been much studied during the past few years in connection with the subject of reaction rates as it is one of the few, and of these the oldest of, unimolecular reactions. In papers dealing with the kinetics of the nitrogen pentoxide reaction, it has ordinarily been assumed to have a molecular diameter of 10^{-7} cm. Recent calculations by Tolman, Yost and Dickinson[1] and by Lewis[2] show that in order for it to be activated sufficiently rapidly it should have the extraordinarily large diameter of 6.07×10^{-6} cm. In this case one of the molecules is activated, which may greatly modify its effective diameter. It seems of interest, however, to determine this value by viscosity measurements.

[3] H. N. Alyea and H. L. J. Bäckström, This Journal, **51**, 90 (1929).

[1] Tolman, Yost and Dickinson, *Proc. Nat. Acad. Sci.*, **13**, 188 (1927).

[2] Bernard Lewis, *Science*, **66**, 331 (1927).