2. The ammono salts, sodium and potassium ammonomagnesiates, react with magnesium in a similar manner to form magnesium amide. This latter substance is likewise formed by the action of the amides of lithium and sodium and a solution of sodium in liquid ammonia on magnesium.

3. The preparation and properties of magnesium amide, $Mg(NH_2)_2$, and sodium ammonomagnesiate, $Mg(NHNa)_2 \cdot 2NH_3$ or $Na_2[Mg(NH_2)_4]$, are described.

4. It is well known that magnesium hydroxide is formed by the action of aqueous solutions of salts of the alkali metals upon magnesium. It is probable that the true mechanism of these reactions—in so far as they do not depend upon electrochemical influences—is the same as that by which magnesium amide—the magnesium hydroxide of the ammonia system—is formed by the action of liquid ammonia solutions of the same salts upon magnesium. For instance, the reaction between an aqueous solution of sodium iodide and magnesium may be represented by the equations, $2NaI + Mg \rightleftharpoons MgI_2 + 2Na; 2Na + 2H_2O = 2NaOH + H_2; 2NaOH + MgI_2 = Mg(OH)_2 + 2NaI$.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

PHOTOCHEMICAL STUDIES. IV. THE THERMAL DECOMPOSITION OF ANHYDROUS OXALIC ACID AND ITS RELATION TO THE PHOTOCHEMICAL DECOMPOSITION

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In a previous article[1] a report was made of a study of the photochemical decomposition of anhydrous oxalic acid. It was found that the anhydrous acid decomposes under the influence of radiation of wave length shorter than about 250 mμ. The presence of water was found to accelerate the reaction markedly. Mention was made of the fact that the wave length found for photochemical decomposition did not agree with that calculated from some rough measurements of the rate of thermal decomposition. Since the limits of the spectral regions used in this early study were only approximate, it was deemed advisable to repeat the work on photochemical decomposition with the aid of a monochromatic illuminator. At the same time, the study of the thermal decomposition has been carried out with more exact apparatus with the purpose of obtaining more direct evidence of the applicability or non-applicability of the radiation hypothesis to the decomposition of a solid body. A brief theoretical discussion will be given in which the question as to whether the radiation hypothesis should be applied to a system of this sort will be raised.

[1] Noyes and Kouperman, THIS JOURNAL, **45**, 1398 (1923).

The study of the thermal decomposition of anhydrous oxalic acid was undertaken because it was hoped that the reaction would prove to be relatively simple. Our hopes were based on the fact that in the temperature range used all of the products of decomposition are gases, which might eliminate the necessity of a consideration of the rate of diffusion of the products through the crystals of the substance remaining in the solid state. As is usually the case in a study of this sort, the reaction has been found to be more complicated than had been hoped. It has been found possible to offer reasonable explanations of the phenomena observed, although we readily admit that other explanations may appear equally plausible.

Part I presents a description of the experimental method used. In Part II we present the results obtained in the study of thermal decomposition. The photochemical decomposition is discussed in Part III while a brief theoretical discussion is given in Part IV.

I. The Experimental Procedure for the Study of the Thermal Decomposition

Fig. 1 shows the type of reaction vessel used.

The tube B is sealed to a vacuum line. The anhydrous solid was placed in the reaction vessel C and the whole evacuated to as low a pressure as could be obtained with a mercury-diffusion pump. The capillary at A was sealed, a stopcock attached to B was closed and the apparatus broken from the vacuum line at a point above the stopcock. The apparatus was then placed in a thermostat that had been regulated previously to the desired temperature. B was again attached to the vacuum line and after evacuation the stopcock was opened. The pressure measurements were made by determination of the outside pressure necessary to cause the mercury in the two arms of the manometer to reach the same level.

The anhydrous oxalic acid was prepared by the same method as that used in the determinations of its vapor pressure.[2]

The measurements of thermal decomposition as here described were carried out in the presence of mercury vapor. It was shown that no appreciable reaction between mercury and the anhydrous oxalic acid or its decomposition products takes place by treatment of some of the material with hydrogen sulfide after a run. No precipitate was formed.

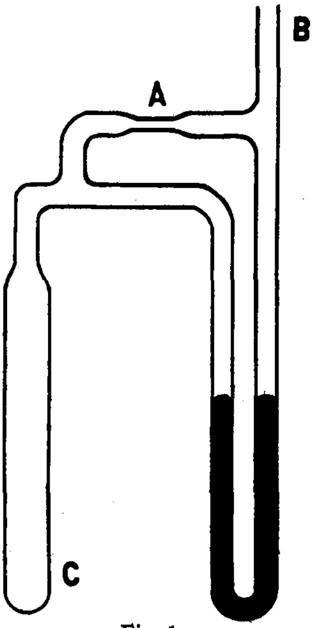


Fig. 1.

Early measurements were carried out in an air furnace capable of regulation to about five-tenths of a degree. There were several disadvantages in this method. In the first place it was found to be difficult to elimi-

[2] Noyes and Wobbe, This Journal, 48, 1882 (1926).

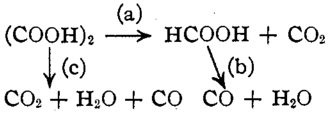
nate temperature gradients, although it was shown that this factor had been successfully controlled in most of the experiments. In the second place, due to the construction of the furnace, it was impossible to place the apparatus in the furnace without destroying the regulation. As a result, temperature equilibrium was slowly attained and the entire apparatus was not uniformly heated during the period of temperature increase. For this reason some of the oxalic acid always sublimed from the solid at the bottom of the reaction vessel and was deposited on the walls of the vessel. This fact is important in the interpretation of some of the data.

The final measurements, and those which were by far more reproducible, were made in a glycerol thermostat capable of regulation[2] to about 0.1°. The temperatures were determined by means of a thermometer which had been compared with a thermometer calibrated by the Bureau of Standards.

The volume of the apparatus was determined from the weight of mercury necessary to fill it.

II. Data on the Thermal Decomposition

Other authors have studied the thermal decomposition of anhydrous oxalic acid.[3] According to the previous work the thermal decomposition proceeds in several different manners. These may be represented schematically as follows.



$$\begin{tikzcd}(COOH)_2 \arrow[r, "(a)"] \arrow[d, "(c)"] & HCOOH + CO_2 \arrow[d, "(b)"] \\ CO_2 + H_2O + CO & CO + H_2O\end{tikzcd} \qquad (1)$$

If the velocity of thermal decomposition is to be determined from measurements of the pressure increase, it is necessary to know whether two molecules or three of decomposition products are formed per molecule of oxalic acid decomposed. Experiments were carried out both at 160° and at 170° with small amounts of material in such a manner that it was possible to let the reaction go to completion. It was thus possible to calculate what the theoretical pressure would be if two molecules of decomposition product were formed per molecule of oxalic acid decomposed and to compare this calculated pressure with the final pressure observed. In the calculation of this final theoretical pressure it must be observed that formic acid is associated in the vapor state.[4] From the data of Ramsperger and Porter it is found that the equilibrium constant $p_M^2/p_B = K = 0.404$ at the boiling point of formic acid, 100.8°; p_M is the pressure in atmospheres of the unimolecular form and p_B is the pressure in atmospheres of the bimolecular form. If 14,500 calories per mole is taken as an average heat of dissociation between the boiling point and the temperatures

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[3] See Beilstein-Prager-Jacobson, "Handbuch der organischen Chemie," Julius Springer, Berlin, **1920**, II, p. 506.

[4] Ramsperger and Porter, This Journal, **48**, 1267 (1926).

studied, it is possible to calculate the values of the equilibrium constant at 160° and 170°. Since one molecule of formic acid and one molecule of carbon dioxide would be formed according to Reaction 1a, it is possible to calculate with the aid of the perfect gas law, $pv = nRT$, the pressure that would be exerted by the carbon dioxide at complete decomposition. If P_{M} and P_{B} are the pressures exerted by the unimolecular form and by the bimolecular form, respectively, in millimeters, it is now possible to set up the following equations,

$$P_{\text{CO}_2} = P_{\text{M}} + 2P_{\text{B}} \tag{2}$$
$$P_{\text{B}} = P_{\text{M}}^2/760\,K \tag{3}$$
$$P_{\text{CO}_2} = 760\ MRT/90.016\ V \tag{4}$$

where M is the weight of oxalic acid taken, 90.016 is the molecular weight of anhydrous oxalic acid and V is the volume of the apparatus. R and T have their usual significance. It is now possible to calculate P_{M} and P_{B}. The pressure to be expected if Reaction 1a is assumed is, therefore,

$$P_{\text{obs.}} = P_{\text{M}} + P_{\text{B}} + P_{\text{CO}_2} + P_{\text{Hg}} \tag{5}$$

where P_{Hg} is the vapor pressure of mercury and is calculated by means of the formula[5]

$$\log P_{\text{Hg}} = 9.9073436 - (3276.638/T) - 0.6519904 \log T \tag{6}$$

Table I presents the data obtained.

Table I

Comparison of Theoretical and Observed Pressures

Absolute temperature	434.5°	444.4°
Volume of vessel	20.40 cc.	20.511 cc.
Weight oxalic acid	0.02225 g.	0.00958 g.
$K = p_{\text{M}}^2/p_{\text{B}}$	6.145	8.934
Vapor pressure Hg	4.43 mm.	6.42 mm.
Press. calcd. (2 molecules)	642.93 mm.	291.25 mm.
Pressure observed	642.2 mm.	294.1 mm.

We feel justified in the assumption that the greater part of the reaction proceeds according to Scheme 1a. It was possible to test this assumption further by immersion of the reaction bulb in liquid air. At the temperature of liquid air both formic acid and carbon dioxide have negligible vapor pressures. There was, however, always some residual pressure. Since, as we will point out later, adsorption of the products is rather high, the agreement in Table I is partly fortuitous. Some carbon monoxide is doubtless formed, although part of the residual pressure may have been due to air adsorbed by the solid.

It is necessary to choose the most plausible type of reaction-velocity equation. Since formic acid decomposes exceedingly slowly in the temperature interval studied,[6] we have based our calculations on the assump-

[5] Menzies, This Journal, **41**, 1786 (1919).

[6] Nelson and Engelder, *J. Phys. Chem.*, **30**, 470 (1926).

tion that two molecules of decomposition product are formed per molecule of oxalic acid decomposed. If the reaction takes place entirely on the surface of the solid, the reaction should really be of "zero" order, unless the surface is proportional to the amount of solid, in which case the reaction would obey a first-order equation. In most of the runs sufficient solid was used so that it would be impossible to decide whether the reaction is of "zero" or first order. When small amounts of solid are used, the reaction is better represented by a "zero" order than by a first-order equation. For small amounts of solid the constants are, however, always high. This can be explained by the fact that the oxalic acid sublimes and condenses in fine crystals on the surface of the glass. As would be expected, the presence of glass wool considerably increases the rate of reaction under these conditions. When larger amounts of material were used, the glass wool was without noticeable effect. We are inclined to the belief that the reaction occurs on the surface of the crystals and is not a decomposition of the vapor, as might be expected from the effect of the glass wool. In fact, it might be difficult to decide between a vapor reaction catalyzed by the glass walls and by the surface of the oxalic acid and a reaction of the solid itself which takes place only on the surface of the crystals.

Several different reaction-velocity equations were tried. Among others an attempt was made to account for the steady increase in constants during the early parts of the runs, particularly at low temperatures. The form of the pressure-time curve could be accounted for by the assumption of two simultaneous reactions, one of the solid and the other of the vapor which is autocatalytic in character. However, when the constants for various runs were compared wide discrepancies were noted and this form of equation was rejected. We will adduce evidence which tends strongly to the assumption that the form of the pressure-time curve is due to adsorption of the products of decomposition, probably of the formic acid.

In the table of data the constants will be given for two different equations. The first is the equation for a first-order reaction and may be written

$$\mathrm{d}p/\mathrm{d}t = k_1\ (p_0 - p) \tag{7}$$

p_0 is the theoretical final pressure which would be exerted at complete decomposition and is calculated from the volume of the apparatus, the weight of material and with the assumption of two molecules of decomposition product per molecule of oxalic acid.

The second equation is of zero order and account is taken of the fact that the formic acid vapor is associated. It will be noted that the two series of constants do not differ greatly. In the derivation of this second equation we proceeded as follows. Let M_0 = initial number of grams of oxalic acid. Then the reaction-velocity equation may be written

$$-\mathrm{d}M/\mathrm{d}t = kM_0 \tag{8}$$

The pressure exerted by the decomposition products will be

$$P = P_{\mathrm{obs.}} - P_{\mathrm{Hg}} - P_{\mathrm{ox}} = P_{\mathrm{M}} + P_{\mathrm{B}} + P_{\mathrm{CO_2}} \qquad (9)$$

where $P_{\mathrm{obs.}}$ is the pressure observed, P_{ox} is the vapor pressure of anhydrous oxalic acid calculated by means of the equation[2] $\log P_{\mathrm{ox}} = 12.2229 - 4726.95/T$. By use of Equations 2 and 3 we find that

$$P = 2P_{\mathrm{M}} + 3P_{\mathrm{B}} = P_{\mathrm{M}}\ (2 + 3P_{\mathrm{M}}/760\ K) \qquad (10)$$

From Equations 4 and 8

$$P_{\mathrm{CO_2}} = P_{\mathrm{M}} + 2P_{\mathrm{B}} = k_0M_0TR760\dot{t}/90.016\ V \qquad (11)$$

and

$$P = P_{\mathrm{CO_2}} + P_{\mathrm{M}} + P_{\mathrm{B}} = 2k_0M_0RT760t/90.016\ V - P_M^2/760 \qquad (12)$$

We now find that

$$P_{\mathrm{M}} = 760K/3\ \left[(1 + 3P/760K)^{1/2} - 1\right] \qquad (13)$$

by solution of the quadratic equation (10). If we substitute in Equation 12 and use the equation between the limits P_2 and P_1 and t_2 and t_1 we find

$$\frac{3}{380K}(P_2 - P_1) - \left[\left(1 + \frac{3}{760K}P_2\right)^{\frac{1}{2}} - \left(1 + \frac{3}{760K}P_1\right)^{\frac{1}{2}}\right] = \frac{9R}{90.016K} \times \frac{M_0\,T}{V} \times k_0(t_2 - t_1) \qquad (14)$$

The values of k_0 are given in the tables.

Table II presents the data obtained in the glycerol thermostat at temperatures from 141.1° to 171.3°. The volumes used in the calculations are the volumes of the apparatus less the volumes occupied by the acid. In order to obtain the latter, two determinations of the density of the anhydrous solid were made at 25°. A saturated solution of anhydrous oxalic acid in anhydrous ether was prepared and the weight of a volumetric flask filled to the mark was obtained. Part of the ether was then displaced by anhydrous solid and the weight again determined. Two determinations gave 1.868 and 1.878 g./cc. as the density of anhydrous oxalic acid. These values are slightly lower than the value 1.900 given in the literature.[7]

TABLE II

REACTION-VELOCITY DATA

Vol. = 14.617 cc. Vol. corr. = 14.511 cc. Wt. = 0.1979 g. $K = P_M/P_B = 8.934$. $T = 171.3°$. $P_{\mathrm{Hg}} = 6.42$ mm. $P_{\mathrm{ox}} = 38.57$ mm. $P_0 = 8439.73$ mm.

$P_{\mathrm{obs.}}$, mm.	Time interval, min.	$k_1 \times 10^3$	$k_0 \times 10^3$
203.6			
330.3	7.933	1.955	1.936
419.3	4.910	2.248	2.142
506.2	5.083	2.144	2.095
584.0	5.263	1.873	1.820
674.9	6.338	1.826	1.772
732.2	3.945	1.877	1.800

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[7] Wagner, *Z. Krystallographie,* **1909,** 471.

TABLE II (*Continued*)

Vol. = 20.650 cc. Vol. corr. = 20.072 cc. Wt. = 1.08214 g. K = 6.1448. T = 161.4°. P_{Hg} = 4.43 mm. P_{ox} = 22.07 mm. P_0 = 32492.6 mm.

$P_{obs.}$, mm.	Time interval, min.	$k_1 \times 10^4$	$k_0 \times 10^4$
111.9			
156.4	12.283	1.19	1.17
195.0	8.116	1.47	1.54
260.5	8.816	2.30	2.42
321.7	5.916	3.21	3.38
377.8	4.566	3.82	4.03
472.8	6.350	4.67	4.94
533.8	4.583	4.16	4.42
603.2	4.623	4.64	4.56
665.2	4.276	4.62	4.93
730.0	4.490	4.54	4.85

Vol. = 16.228 cc. Vol. corr. = 16.059 cc. Wt. = 0.31639 g. K = 6.1448. T = 161.4°. P_{Hg} = 4.43 mm. P_{ox} = 22.07 mm. P_0 = 11889.8 mm.

106.1			
177.4	19.280	3.15	3.16
238.9	10.396	5.06	5.09
356.8	18.830	5.40	5.43
434.0	13.156	5.11	5.12
502.3	12.286	4.87	4.88
580.5	14.785	4.66	4.67
634.3	10.388	4.59	4.59
709.4	15.045	4.45	5.02

Vol. = 18.904 cc. Vol. corr. = 18.387 cc. Wt. = 0.9675 g. K = 3.9879. T = 150.5°. P_{Hg} = 2.88 mm. P_{ox} = 11.58 mm. P_0 = 30903.7 mm.

		$k_1 \times 10^5$	$k_0 \times 10^5$
44.1			
76.9	56.33	1.89	1.90
115.6	55.91	2.25	2.27
156.9	37.83	3.55	3.60
217.4	33.91	5.81	5.92
306.4	26.33	11.0	11.3
394.0[a]	37.58	7.6	7.9
515.5	37.42	10.7	11.1
646.0	40.91	10.5	11.0
716.9	22.66	10.4	10.9

[a] Temperature low.

Vol. = 20.60 cc. Vol. corr. = 19.57 cc. Wt. = 1.92537 g. K = 3.363. T = 146.33°. P_{Hg} = 2.43 mm. P_{ox} = 8.96 mm. P_0 = 57072.94 mm.

45.9			
85.9	69.58	0.91	1.01
108.6	36.33	1.10	1.11
134.8	41.25	1.12	1.13
168.8	39.25	1.52	1.55
201.7	29.58	1.96	2.01
265.2	40.66	2.75	2.94
390.1	51.50	4.28	4.37
502.6	32.58	6.10	6.39
550.1	12.66	6.64	6.56

TABLE II (*Concluded*)

Vol. = 20.94 cc. Vol. corr. = 19.724 cc. Wt. = 2.2812 g. K = 3.246. T = 145.5°. P_{Hg} = 2.35 mm. P_{ox} = 8.33 mm. P_0 = 67102.02 mm.

$P_{obs.}$, mm.	Time interval, mm.	$k_1 \times 10^5$	$k_0 \times 10^5$
54.5			
84.4	73.58	0.61	0.61
103.0	44.08	.63	.64
129.2	58.16	.67	.69
151.3	36.83	.90	.92
182.0	40.00	1.15	1.18
229.7	43.41	1.64	1.69
265.7	24.25	2.22	2.15
340.6	39.33	2.85	3.08
417.1	30.91	3.71	3.90
451.0	12.20	4.17	4.40
473.3	7.63	4.38	4.64
541.2	21.75	4.69	4.98

Vol. = 16.314 cc. Vol. corr. = 16.159 cc. Wt. = 0.2895 g. K = 2.698. T = 141.1°. P_{Hg} = 1.95 mm., P_{ox} = 6.47 mm. P_0 = 10200.25 mm.

18.8			
27.5	64.39	1.32	1.32
34.7	52.61	1.33	1.34
44.3	79.30	1.18	1.19
57.4	90.00	1.42	1.43

Fig. 2 shows a plot of log k_1 against $1/T$. Table III shows a comparison between the observed values and values calculated by means of the equation log k_1 = $22.859-11370/T$.

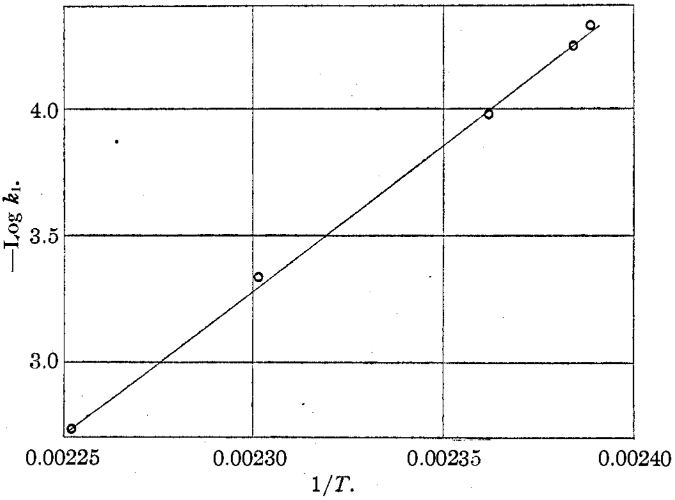

Fig. 2.

Table IV shows a comparison of the values of k_0 obtained experimentally and the values obtained by means of the equation log $k_0 = 22.548-11227/T$.

TABLE III

SUMMARY OF CONSTANTS FOR FIRST-ORDER EQUATION

T, °C.	k_1 (calcd.)	k_1 (found)	Remarks
171.3	1.88×10^{-3}	1.99×10^{-3}	Av. all consts.
161.4	4.91×10^{-4}	4.53×10^{-4}	Av. last five
		4.88	Av. last seven
150.5	1.05×10^{-4}	1.09×10^{-4}	Av. of four, omit one, temp. low
146.33	5.64×10^{-5}	5.77×10^{-5}	Av. last three
145.5	4.98 "	4.69 "	Highest const.
141.1	2.56 "	1.31 "	Av. all consts.

TABLE IV

SUMMARY OF CONSTANTS FOR ZERO-ORDER EQUATION

T, °C.	k_0 (calcd.)	k_0 (found)	Remarks
171.3	1.93×10^{-3}	1.93×10^{-3}	Av. all consts.
161.4	5.12×10^{-4}	4.74×10^{-4}	Av. last five
		4.97 "	Av. last seven
150.5	1.11 "	1.11 "	Av. of four, omit one, temp. low
146.33	6.04×10^{-5}	6.56×10^{-5}	Highest const.
145.5	5.35 "	4.98 "	Highest const.
141.1	2.77 "	1.32 "	Av. all consts.

It will be seen upon inspection of the data that at the lower temperatures the constants continually increase with time. Also at 161.4° the period of increase is longer when a large amount of acid is used and the final value attained is somewhat smaller when 1.08214 g. of material is used than when 0.31639 g. of material is taken. These facts suggest strong adsorption of the products of the reaction by the glass and also by the acid itself. It is a well known fact that formic acid is very highly adsorbed by glass. If this is the case, constants at lower temperatures should be about half the calculated values. This is found to be the case at 141.1° and at 131.4° (data not shown). Additional evidence in favor of the assumption that deviations are due to adsorption is obtained from two other sources. Two runs (data not shown) were made at 141.2°, one with as much as 7 g. of material. Constancy was not attained and the final constant was even lower than that obtained with a small amount of material. Several experiments were made at 161.4° in the presence of glass wool and with small amounts of material. The final pressures attained were about half those calculated on the basis of two molecules of decomposition product per molecule of oxalic acid. These facts indicate that in the presence of a large surface nearly all of the formic acid and probably some of the carbon dioxide are adsorbed.

The data obtained in the air furnace are in general agreement with the above, although the experimental error was considerably larger. At the higher temperatures the constants obtained in the air-furnace runs are always higher than those obtained in the glycerol thermostat. As we have already pointed out, this can be most reasonably explained due to the non-uniform heating and consequent sublimation.

Experiments with very small amounts of material gave uniformly high results, and glass wool causes the reaction to proceed much more rapidly. Experiment with a larger amount of solid at 145° failed to show any appreciable effect of the glass wool. It is probable when a small amount of material is used that practically all of the acid vaporizes and condenses on the glass wool which would heat more slowly. When a large amount of material is used, the early constants should be high until the sublimed acid is used up and subsequently the normal rate should be observed. This seems the most logical explanation of the data at 171.3° in which there is a slight decrease in the constants after the first few minutes. An air-furnace run at 170.3° of only 12 minutes' duration gave two constants about 50% higher than those calculated.

III. The Photochemical Decomposition

The results reported in the previous paper[1] have, in general, been confirmed. The photochemical decomposition was carried out by means of radiation from a carbon-arc lamp, the electrodes of which had been impregnated with salts of various heavy metals. A monochromatic illuminator was used to isolate various parts of the spectrum.

At first it appeared that there were two regions of photochemical decomposition, the first in the neighborhood of 300 mμ and the second below 250 mμ. The first of these regions was not noted in the previous work. Upon continued evacuation less and less effect was observed at 300 mμ and the effect at wave lengths below 250 mμ also decreased markedly in magnitude. This decrease in effect is to be ascribed to the removal of some impurity, presumably water, by continued evacuation. As noted in the previous work, there is a period of induction and this period becomes longer and longer the more the system is evacuated. According to Berthelot and Gaudechon the photochemical decomposition of anhydrous oxalic acid yields first formic acid and carbon dioxide, long waves changing the former into carbon monoxide and water and short waves into carbon dioxide and hydrogen.[8] Water may be one of the products of the reaction so that the reaction would be autocatalytic if affected by water.

The reaction is exceedingly slow and since the intensity of the light transmitted by the monochromatic illuminator is small, the results should be considered as somewhat doubtful. As a rough check the monochromator was removed. A stream of water was allowed to run over the window of the reaction vessel to prevent heating. Decomposition took place at about the same rate as that obtained in the previous work.[1] With a

[8] Berthelot and Gaudechon, *Compt. rend.*, **158**, 1791 (1914). See also Ref. 4.

plate of Pyrex glass interposed, the decomposition became immeasurably slow. Since Pyrex transmits well to 300 mμ and somewhat more faintly to about 285 mμ, the results of this experiment are in qualitative agreement with the statements made in the previous article.

Light in the visible spectrum was apparently without effect on the anhydrous acid.

IV. Theoretical Discussion

By use of the formula of the simple radiation hypothesis, $d\ ln\ k/dT = Nh\nu/RT^2$, it is found that radiation of wave length between 500 and 600 mμ should cause photochemical decomposition. Since this type of radiation is not active, we may inquire briefly into possible mechanisms of activation.

If the reaction is purely a surface reaction as we have indicated for the thermal reaction it might be supposed that the amplitude of vibration was the critical factor in the thermal decomposition. Since formic acid is the main product, the reaction leads to a rupture of the carbon to carbon bond in the oxalic acid. It is conceivable that this might be brought about for surface molecules while molecules in the interior of the crystals would be held under closer constraint. The data on the crystal structure of anhydrous oxalic acid[9] indicate that four molecules make up the crystal unit. Current theories with regard to the specific heats of solid bodies would justify the supposition that amplitudes of vibration are larger at higher temperatures. If a certain amplitude of vibration were necessary as a prerequisite for decomposition, then the vibrators could attain a given quantized state by the absorption of infra-red quanta. The wave length calculated by the simple radiation hypothesis could scarcely have any definite meaning under these conditions. It may be objected that if this hypothesis is accepted, infra-red radiation should have a marked effect on the rate of reaction, whereas in the case of nitrogen pentoxide this has been shown not to be the case.[10] No satisfactory solution of this difficulty has yet been presented. Loss of energy by collision of the second kind before decomposition can take place might possibly explain the lack of effect of infra-red radiation. The infra-red radiation would lead to an increase in temperature rather than direct decomposition. The effect of the infra-red radiation would be small unless an appreciable proportion of the molecules were in quantized states near those necessary for decomposition. This explanation can scarcely account for the observed facts in the case of nitrogen pentoxide. There is also the possibility that infra-red radiation does not produce the same type of vibration within the molecule as increase in temperature. Taylor[10] has suggested that vibration may be the important factor in chemical reactions, although it is admittedly difficult to ac-

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[9] Hoffmann and Mark, *Z. physik. Chem.*, **111**, 321 (1924).

[10] Taylor, THIS JOURNAL, **48**, 577 (1926). Daniels, *ibid.*, **48**, 607 (1926).

count for the restoration of the Maxwell distribution without the aid of radiation. The assumption of the important role played by vibration has some merit in the case under consideration if the reaction is a surface reaction, since molecules below the surface of the crystals may not be able to attain sufficient amplitude of vibration to cause decomposition.

If attention is now turned to the photochemical decomposition, it seems probable that the mechanism of activation is not the same as for the thermal reaction. Ultraviolet radiation of wave lengths such as those which cause photochemical decomposition probably does more than increase the energy of vibration. Effects of this type of radiation are best explained by introduction of electron rearrangements in addition to vibration. In this case the reaction might not be purely a surface phenomenon. Evidence in favor of this assumption may be obtained from the fact that the pressure continues to increase after the light is shut off. As suggested in the previous article, diffusion of the products through the crystal lattice may account in part for the induction period. Similarly we are not inclined to introduce any chain mechanism to explain the phenomenon here observed but are inclined to ascribe it to diffusion. It is impossible as yet to say much about the motions of electrons in molecules, but it is not unreasonable to expect that certain electron rearrangements might involve an instability which would lead to decomposition.

Summary

1. The thermal decomposition of anhydrous oxalic acid has been studied in the temperature range 130–170°. The reaction proceeds mainly to give formic acid and carbon dioxide.

2. The reaction probably takes place entirely on the surface of the crystals and the state of subdivision therefore influences the rate of reaction.

3. The reaction is nearly of "zero" order, since the surface of the solid would not change greatly under the conditions of experiment. The constants for zero-order equation may be expressed by the equation $\log k_0 = 22.548 - 11227/T$.

4. The critical increment is found to be 51,400 calories. This value is somewhat in doubt due to the fact that adsorption of the decomposition products is very high and pressure measurements may not give an accurate value of the rate of reaction.

5. The wave length predicted by the radiation hypothesis is about 550 mμ. This is found to be without measurable effect.

6. Previous work is confirmed and decomposition of the anhydrous solid is brought about by radiation of wave length about 250 mμ or below.

7. It is thought probable that the mechanism of activation is not the same for the thermal and photochemical reactions and the question is

raised as to whether this reaction affords a good test of the radiation hypothesis.

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THE POTENTIAL OF THE FLUORINE ELECTRODE FROM THERMAL DATA

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The recent determinations of v. Wartenberg[1] of the heats of two reactions involving fluorine, together with the values of Latimer and Buffington[2] for the ionic entropies, permit the calculations of a new value of the potential of the fluorine electrode, long a quantity of much uncertainty. The reactions studied and their heats are

$$\tfrac{1}{2}H_2 + \tfrac{1}{2}F_2 = HF_{sol};\ \Delta H = -75.6 \text{ kg. cal.} \qquad (1)$$

$$Cl^- + \tfrac{1}{2}F_2 = F^- + \tfrac{1}{2}Cl_2;\ \Delta H = -39.9 \text{ kg. cal.} \qquad (2)$$

The calculations in this article will show that these heats lead to concordant values for the fluorine electrode almost a volt higher than the value estimated from the heat of formation of hydrogen fluoride by Berthelot and Moissan.[3]

The concentration of hydrogen fluoride in Reaction 1 was one mole in 400 moles of water. Even at this dilution, hydrogen fluoride is far from complete ionization, as is shown by the fact that its heat of neutralization is about 3000 cal. more than that of typical strong acids. Since we have insufficient data to calculate the entropy and free energy of dissociation of hydrogen fluoride in solution we shall not attempt to use Equation 1 directly, but shall use the values for the heat of formation of the metal fluorides derived from it by combination with data for the heat of formation of the metal oxides and their heats of neutralization by hydrogen fluoride. These values have been calculated by v. Wartenberg[4] and are given in the first column of Table I. The entropy of the reactions for the formation of the metal fluorides in solution may be calculated from the values for the entropies of the metals, their ions, fluorine gas and fluoride ions. These values, tabulated in Table I, have been taken from papers by Lewis, Gibson and Latimer,[5] and by Buffington and Latimer,[6] with the exception of the value for fluorine, which has been taken in agreement with the Tetrode equation[7] in the modified form given by Latimer.[8]

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[1] v. Wartenberg, *Z. anorg. allgem. Chem.*, **151**, 313 (1926).

[2] Latimer and Buffington, THIS JOURNAL, **48**, 2297 (1926).

[3] Berthelot and Moissan, *Ann. phys. chim.*, [6] **23**, 570 (1891).

[4] Ref. 1, p. 326.

[5] Lewis, Gibson and Latimer, THIS JOURNAL, **44**, 1008 (1922).

[6] Buffington and Latimer, *ibid.*, **48**, 2305 (1926).

[7] Tetrode, *Ann. Physik*, **33**, 434 (1912).

[8] Latimer, THIS JOURNAL, **43**, 818 (1921).