equation of state, and recently derived by Heitler upon different assumptions, is applied to a large number of solutions with very satisfactory results.

3. The equation is applied to the calculation of other properties dependent upon activity, including the e.m.f. of concentration cells, the heat of solution of solids, the expansion on mixing and the Gibbs adsorption equation.

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PHOTOCHEMICAL STUDIES. VIII. THE PHOTOCHEMICAL DECOMPOSITION OF MALONIC ACID BOTH IN THE PRESENCE AND ABSENCE OF URANYL SULFATE

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The photochemical decompositions of many organic acids have been studied in some detail. Of these none has received more attention than the decomposition of oxalic acid. It is not necessary, at the present time, to summarize all of the work that has been done.[1] Earlier work on the nature of the products formed has been shown by Allmand and Reeve[2] not to agree with the composition of the products formed during the early stages of the reaction. These authors show that the principal reaction consists in the formation of formic acid and carbon dioxide. Since the former may be decomposed photochemically, other products would result with long exposures. They found, further, that the quantum efficiency varied with wave length, the highest value obtained being 1/100 at 265 mμ. Anderson and Robinson[3] report an average yield of 1/1392 molecule per quantum for radiation from a quartz mercury arc lamp.

The photochemical decomposition of oxalic acid sensitized by uranyl salts has also received considerable attention. Measurements of quantum efficiency of the sensitized reaction are somewhat at variance, but the best evidence indicates that the value is approximately one.[4,5] Büchi,[4] from a consideration of his determinations of the rate of photochemical decomposition of oxalic acid in solutions of varying concentration and with various amounts of uranyl sulfate, has come to the conclusion that a complex molecule, or a molecule of uranyl oxalate, is the photosensitive mole-

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[1] Kistiakowsky, "Photochemical Processes," The Chemical Catalog Co., Inc., New York, **1928**, pp. 146, 229, has given a partial summary of recent work on this reaction.

[2] Allmand and Reeve, *J. Chem. Soc.*, **129**, 2834 (1926).

[3] Anderson and Robinson, THIS JOURNAL, **47**, 718 (1925).

[4] Büchi, *Z. physik. Chem.*, **111**, 269 (1924).

[5] Bowen and Watts, *J. Chem. Soc.*, **127**, 1607 (1925).

cule in the reacting system. He further supports this conclusion by the data of Henri and Landau,[6] which show that the absorption coefficients of oxalic acid and uranyl salts are not additive in solutions containing both substances, but that a marked increase in the absorption of uranyl sulfate solutions is brought about by the addition of small amounts of oxalic acid. As pointed out by Kistiakowsky,[1] there is further evidence in favor of the sensitivity of the complex in the comparison of the quantum efficiencies with and without catalyst.

Corresponding work on other acids has been attempted. Thus Müller[7] has found that approximately one molecule of lactic acid was decomposed per quantum absorbed in the presence of uranyl sulfate. Bolin[8] found, however, that uranyl salts in the presence of lactic acid are quantitatively reduced. The rate of reaction reached a steady value with increase in concentration of uranyl sulfate. No evidence for or against complex formation is contained in either of these papers.

Some work has been done on the photochemical decomposition of malonic acid. Fay[9] in the presence of catalyst, found that the rate of decomposition in sunlight was exceedingly slow. Kailan[10] found that more carboxyl groups were decomposed in the case of malonic acid than in the case of oxalic acid when the two were exposed to full radiation from a quartz mercury arc lamp. Berthelot and Gaudechon[11] found that uranyl salts acted as catalysts in the photochemical decomposition of malonic acid. Volmar[12] states that the main products of the photochemical decomposition of malonic acid are acetic acid and carbon dioxide.

The present work was undertaken with the object of determining the possible mechanisms of the action of uranyl sulfate in catalyzing the photochemical decomposition of malonic acid.

I. Experimental Procedure and Results

In all of the work which follows the amount of decomposition of malonic acid was determined by titration with sodium hydroxide solutions (free from carbonate) with the use of phenolphthalein as the indicator. The solutions were boiled to remove carbon dioxide. In solutions containing uranyl sulfate (below 0.01 *M*), the uranyl sulfate titrated toward phenolphthalein as though it were an equivalent amount of sulfuric acid. This point was repeatedly checked by making up solutions containing a known weight per unit volume of $UO_2SO_4 \cdot 3H_2O$. The amount of decomposition

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[6] Henri and Landau, *Compt. rend.*, **158**, 181 (1913).

[7] Müller, *Biochem. Z.*, **178**, 77 (1926).

[8] Bolin, *Z. physik. Chem.*, **87**, 490 (1914).

[9] Fay, *Am. Chem. J.*, **18**, 269 (1896).

[10] Kailan, *Monatsh.*, **34**, 1209 (1913).

[11] Berthelot and Gaudechon, *Compt. rend.*, **157**, 333 (1923).

[12] Volmar, *Compt. rend.*, **180**, 1172 (1925).

agreed roughly with that determined by gas evolution, but the latter method of measurement was not considered to be as accurate as the titration method.

(a) **Analysis of the Gas Evolved during Decomposition.**—A solution of malonic acid was placed in a quartz reaction vessel sealed to a Toepler pump by means of a graded seal. The solution was outgassed as thoroughly as possible and then exposed to the full radiation from a quartz mercury arc lamp. The evolved gases were pumped off and collected in a small test-tube over mercury. The gases were then analyzed by the micro method of Reeve.[13] The total volume was measured in a capillary tube. The gas was swept into the test-tube again and a small piece of fused potassium hydroxide introduced to absorb the carbon dioxide. The residual gas was measured in the capillary tube. An attempt was made to analyze the residual gas by sparking with air, but no contraction (beyond experimental error) was noticed. After sparking the gas was again tested for carbon dioxide but no further absorption was found. Sparking alone, without admixture of air, did not produce any consistent change in volume. This probably indicates that no appreciable quantity of methane or carbon monoxide is formed. Table I presents the results obtained. The residue seems to be largely air.

TABLE I

ANALYSIS OF THE GAS FORMED DURING PHOTOCHEMICAL DECOMPOSITION OF MALONIC ACID

Concn. of malonic acid, 0.05 M. 1 cm. = 0.0227 cc.

Conditions	Total gas, cm.	Residue, cm.	CO_2 by vol., %
No catalyst	12.6	0.7	94.5
No catalyst	10.0	.4	96.0
No catalyst	16.2	.7	95.7
No catalyst	18.6	.75	96.0
Catalyst 0.005 *M*	54.5	2.3	96.0
Same (Pyrex vessel)	80.0	0.4	99.5

It is probable that the difference between the last analysis and the others is due to more thorough outgassing in the Pyrex vessel.

We feel safe in stating that the early stages of malonic acid decomposition lead almost exclusively to the formation of carbon dioxide and acetic acid. This seems to be true both in the presence and absence of catalyst and in the presence of catalyst whether the full mercury arc spectrum is used or just those wave lengths longer than 300 $m\mu$.

(b) **Effect of Uranyl Sulfate on the Rate of Photochemical Decomposition with Radiation from the Full Mercury Arc.**—A series of decompositions was carried out in which solutions 0.05 *M* with respect to malonic acid and containing various concentrations of uranyl sulfate were exposed to radiation from the full mercury arc in a vessel open to the air. It was shown that the rate was practically the same in the absence of air by carrying out a few experiments in a closed vessel evacuated to the vapor pressure of water over the solution. The determinations were made by titration (see above). Table II (see also Fig. 1) shows the relative rate of decomposition with varying concentration of catalyst. The values are averages of three determinations.

(c) **The Determination of the Quantum Efficiency.**—The light intensities were all measured by means of a thermopile calibrated by a standard source of radiation

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[13] Reeve, *J. Chem. Soc.*, **125**, 1946 (1924).

Table II

Effect of Catalyst on the Reaction Rate

Concn. of UO_2SO_4 (*M*)		0.0000	0.0002	0.0005	0.0010	0.0025	0.005	0.010
Rel. reac. rate		.33	.58	.62	.85	1.02	1.01	.97
Rel. rate calcd. by eq. (1)		.33	.50	.68	.85	0.98	1.00	1.00
Rel. rate calcd. by eq. (2)	I	.33	.52	.68	.88	1.04	1.01	0.84
	II	.33	.55	.65	.85	1.06	1.01	.73

furnished by the Bureau of Standards; 1 cm. deflection corresponded to 2.0 ergs per mm.^{2} per second.

The percentage absorption was determined by a modification of the procedure used by Herr and Noyes.[14] A perforated plate was placed in front of a quartz mercury arc lamp. The radiation was made into a slightly diverging beam by means of a quartz lens and then passed through a water cell about 3.2 cm. in thickness. The absorption cell containing water was then fixed in such a way that it could be interposed between the water cell and the thermopile. After the decrease in deflection due to interposition of the cell filled with water had been determined, the cell was filled with the solution to be studied and the decrease in deflection again determined. The difference between the two percentage decreases was taken as the percentage of the radiation absorbed by the solution.

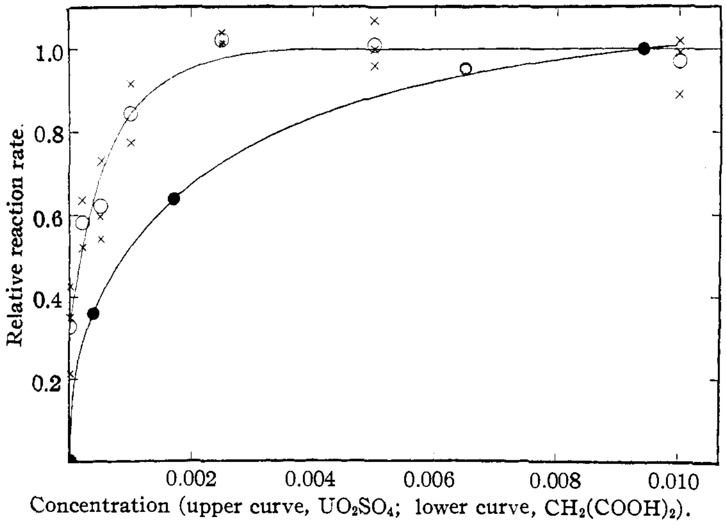

Fig. 1.—Upper curve is that of Equation 1. Crosses are observed values, circles are average values. The concentration of $CH_2(COOH)_2$, is 0.05 *M*. Through quartz. The lower curve shows the variation in rate with concentration of malonic acid (see Table VII). Concentration of UO_2SO_4 is 0.01 *M*. Through Pyrex glass.

The actual determination of the amount of decomposition required a more intense radiation than could be obtained by the system described in the preceding paragraph. The radiation was passed (without a lens) through an opening about two centimeters in diameter, through the water cell and then through the solution to be studied. The

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[14] Herr and Noyes, This Journal, **50**, 2345 (1928).

intensity of the incident radiation was obtained by placing the thermopile in the position to be occupied by the reaction vessel. The value of the incident intensity and the percentage absorption together with the amount of decomposition permitted a calculation of the quantum efficiency, providing the average wave length of the radiation were determined. From a consideration of the absorption coefficients of malonic acid as determined by Bielecki and Henri[15] and the distribution of the intensity of the radiation from the mercury arc given by Reeve,[16] the average wave length was calculated to be 250 mμ in the absence of catalyst. In the presence of catalyst, absorption was assumed to be complete for lines below 320 mμ and the average wave length was calculated to be 290 mμ. Both of these values should be good to about 10 mμ, although it is recognized that the intensity distribution given by Reeve would probably not imply high accuracy to the lamp used in these experiments. That they were in approximate agreement was ascertained by the use of a monochromatic illuminator with the thermopile. For radiation transmitted by Pyrex, the average wave length absorbed in the presence of catalyst was taken as 320 mμ. The absorption of the Pyrex plate used was determined with a spectrograph and rotating sector. Log $I/I_0 = -0.5$ at 313 mμ and -1.2 at 301 mμ. Thus very little radiation below 300 mμ was transmitted. The following tables show the data obtained.

TABLE III

THE QUANTUM EFFICIENCY OF THE PHOTOCHEMICAL DECOMPOSITION OF MALONIC ACID WITHOUT CATALYST

(Concn., 0.05 *M*)

Duration of run, hours	5.4	6.67	7.25
Fraction absorbed	0.031	0.031	0.031
Ergs. absorbed × 10^{-8}	4.225	5.98	1.78
Amt. decomposed (cc. of NaOH)	1.49	1.80	0.55
Normality of NaOH	0.0481	0.0481	.0481
Molecules decomp. × 10^{-19}	4.35	5.24	1.60
Molecules per erg × 10^{-11}	1.03	0.876	0.899
Average wave length, mμ	250	250	250
Quantum efficiency	0.81	0.68	0.71 av. 0.73

(Since the fraction 0.031 is the difference between 0.110 ± 0.005 and 0.141 ± 0.005, the average quantum efficiency is 0.73 ± 0.25.)

TABLE IV

THE QUANTUM EFFICIENCY OF THE PHOTOCHEMICAL DECOMPOSITION OF MALONIC ACID WITH CATALYST

Malonic acid, 0.05 *M*. Uranyl sulfate, 0.005 *M*

Duration of run, hours	5.3	3.5	3.5
Fraction absorbed	0.276	0.276	0.276
Ergs. absorbed × 10^{-8}	38.4	24.9	23.8
Amt. decomposed (cc. of NaOH)	5.35	5.05	4.45
Normality of NaOH	0.0481	0.0327	0.0327
Molecules decomposed × 10^{-19}	15.57	10.0	8.81
Molecules per erg × 10^{-11}	0.416	0.402	0.370
Average wave length, mμ	290	290	290
Quantum efficiency	0.28	0.27	0.25 av. 0.27

The fraction 0.276 should be accurate to ±0.02. The quantum efficiency is 0.27 ± 0.02.

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[15] Bielecki and Henri, *Ber.*, **45**, 2819 (1912).

[16] Reeve, *J. Phys. Chem.*, **29**, 34 (1925).

Table V

The Quantum Efficiency of the Photochemical Decomposition of Malonic Acid with Catalyst and a Pyrex Filter Interposed

Malonic acid, 0.05 *M*. Uranyl sulfate, 0.005 *M*

Duration of run, hours	7.3	6.0	4.0
Fraction absorbed	0.160	0.112	0.112
Ergs. absorbed $\times 10^{-8}$	20.5	9.26	8.66
Amt. decomposed (cc. of NaOH)	4.05	1.92	1.83
Normality of NaOH	0.0327	0.0327	0.0327
Molecules decomp. $\times 10^{-19}$	8.02	3.80	3.82
Molecules per erg $\times 10^{-11}$	0.390	0.411	0.442
Average wave length, mμ	320	320	320
Quantum efficiency	0.24	0.25	0.27 av. 0.25

The fractions absorbed should be accurate to ±0.02. The average quantum efficiency is 0.25 ± 0.04.

Since the thermopile was calibrated for relatively feeble light intensities and used for high light intensities in the above experiments, the question might arise as to the validity of the light intensity measurements. To test this point a 1000-watt lamp was used and the inverse square law assumed. It was found that within the accuracy of the application of the inverse square law, the measurements of the high light intensities by the thermopile were justified.

(d) **Determination of Absorption Coefficients.**—It has already been pointed out that Henri and Landau[6] have shown that the addition of small amounts of oxalic acid to uranyl sulfate causes a marked increase in the absorption coefficients. This is, in general, good evidence for the formation of a complex. Similar experiments were carried out with malonic acid using a rotating sector in conjunction with a spectrograph. Absorption coefficients for the uranyl sulfate alone were in approximate agreement (although slightly higher) with those of Henri and Landau. Addition of malonic acid did not produce a change greater than the experimental error. A solution containing both malonic acid and uranyl sulfate showed nearly the same absorption as a solution of malonic acid placed in series with a solution of uranyl sulfate in such a manner that the total number of molecules traversed by the radiation was the same. We find, therefore, no evidence for or against complex formation from this source.

(e) **Effect of the Addition of Sulfuric Acid.**—Two solutions, each 0.05 *M* with respect to malonic acid, to one of which was added 0.005 *M* sulfuric acid, were exposed under identical conditions to radiation from a quartz mercury arc lamp. The amounts of decomposition were identical within about 2%.

(f) **Effect of Variation of the Malonic Acid Concentration with Constant Concentration of Uranyl Sulfate.**—Six test-tubes (Pyrex) were filled with ten cc. each of solutions made up to 0.01 *M* with respect to uranyl sulfate and with varying amounts of malonic acid. Three concentrations were used so that duplicates were made of each determination. In addition one tube was filled with a solution 0.01 *M* with respect to uranyl sulfate and 0.05 *M* with respect to oxalic acid. The tubes were rotated in regular order before a quartz mercury arc lamp (without water filter) so that each received the same extent of illumination. The oxalic acid (since it decomposed more rapidly than the malonic acid) and one solution of malonic acid were exposed for a shorter time than the others. Table VI shows the data for these two tubes which were titrated early.

As will be seen in Table VII, a similar solution with 0.1 *M* malonic acid decomposes 1.58 times as rapidly as 0.02 *M* malonic acid. If it is assumed that the light absorbed by the malonic acid-uranyl sulfate solution is the same as for the oxalic acid-uranyl

TABLE VI

COMPARISON OF RATE FOR OXALIC AND MALONIC ACIDS IN THE PRESENCE OF URANYL SULFATE

$KMnO_4$, 0.1050 *N*. NaOH, 0.0327 *N*. Solution I, 0.01 *M* UO_2SO_4, 0.05 *M* $H_2C_2O_4$. Solution II, 0.01 *M* UO_2SO_4, 0.02 *M* $HO_2CCH_2CO_2H$.

Solution I		Solution II	
Cc. $KMnO_4$ (blank)	9.72	Cc. NaOH (blank)	19.06
Cc. $KMnO_4$ (after exposure)	5.25	Cc. NaOH (after exposure)	18.00
Difference	4.47	Difference	1.06
Moles $H_2C_2O_4$ decomposed	0.000235	Moles malonic acid decomposed	0.0000347

sulfate solution and that the quantum efficiency for the decomposition of the latter is one,[4] the quantum efficiency for the decomposition of malonic acid (0.1 *M*) in the presence of uranyl sulfate 0.01 *M* is found to be 0.23, which is in good agreement with the values given in Table V.

Since the oxalic acid solution probably absorbs more than the malonic acid solution, this figure is too low rather than too high. Table VII shows the variation of rate of decomposition with concentration of malonic acid with constant concentration of uranyl sulfate.

TABLE VII

VARIATION OF RATE WITH CONCENTRATION OF MALONIC ACID

NaOH, 0.0327 *N*. Solutions all 0.01 *M* in UO_2SO_4. Solution III, 0.10 *M* in malonic acid, Solution IV, 0.02 *M* in malonic acid, Solution V, 0.005 *M* in malonic acid.

Solution	NaOH (blank), cc.	NaOH (after exposure), cc.	Diff. (av.)	Rel. rate
III	66.90	64.55		
	67.01	64.53	2.41	1.00
IV	19.06	17.53	1.53	0.64
	19.06			
V	10.24	9.35	0.86	0.36
	10.15	9.34		

(g) **Effect of Pyrex on the Rate of Decomposition of Malonic Acid without Catalyst.**—One experiment was carried out with a Pyrex filter in the absence of catalyst. Decomposition was observed at about one-sixth the rate without Pyrex. Attempts to measure the light absorption failed, however, as the amount of light absorbed by the solution was so slightly different from that absorbed by water. This may be taken to indicate that the quantum efficiency for the pure acid is not greatly variable with frequency.

II. Discussion of Results and Conclusions

We may summarize the results reported above as follows. 1. The decomposition of malonic acid, both with and without addition of uranyl sulfate, gives carbon dioxide and acetic acid.

2. The rate of decomposition in the presence of radiation from a mercury arc lamp increases with addition of uranyl sulfate and approaches a constant value. The average rates indicate a slight falling off when the concentration of uranyl sulfate exceeds about 0.005 *M*, but this falling off is smaller than the experimental error.

3. The quantum efficiency of the catalyzed reaction is smaller than for the uncatalyzed reaction.

4. With constant uranyl sulfate concentration, the rate of photochemical decomposition of malonic acid decreases with the decrease in malonic acid concentration. However, the rate is not proportional to the malonic acid concentration but varies approximately as the cube root of the latter.

5. There is no evidence which indicates a complex molecule, with the possible exception of the observation by Fay[9] that uranyl malonate is soluble in an excess of malonic acid.

6. In view of the fact that addition of sulfuric acid produces no marked change in rate of decomposition, the extent of ionization of the malonic acid does not make an appreciable difference.

7. The effect of wave length on the quantum efficiency is not marked.

It is of interest to ascertain what type of equation will satisfactorily reproduce the effect of uranyl sulfate on the reaction rate. Since the malonic acid concentration was kept constant during these runs, there is only one variable concentration to consider. In Table II are given values calculated by means of the following equation

$$-\mathrm{d}[\mathrm{H_2Ma}]/\mathrm{d}t = K_1I_0(1 - 10^{-kCl}) + K_2 10^{-kCl} \qquad (1)$$

where $[H_2Ma]$ represents the concentration of malonic acid, C is the concentration of uranyl sulfate in millimoles per liter, l is the thickness of the solution (here kept constant), I_0 is the incident intensity, k is the absorption coefficient of the uranyl sulfate and K_1 and K_2 are constants. The values in Table II (see also Fig. 1) were obtained by using $K_1I_0 = 1.00$, $K_2 = 0.327$, $kl = 0.64$; l was about 2 cm. in these experiments, so that the absorption coefficient is rather high. However, monochromatic light was not used and the absorption coefficient of uranyl sulfate increases very rapidly below 330 mμ.[6]

Equation 1 may be derived by assuming that there are two independent reactions, one due to the light absorbed by the catalyst and the other due to the light absorbed by the malonic acid. The first term on the right-hand side of the equation would represent the rate of the former reaction and the second term the rate of the latter. $1-10^{-kCl}$ would represent the fraction of the light absorbed by the catalyst and 10^{-kCl} would represent the fraction unabsorbed. Of the latter a definite fraction would be absorbed by malonic acid since its concentration is maintained constant in all runs.

With the values chosen, Equation 1 shows that the relative reaction rate should approach unity asymptotically. The fact that such small concentrations of uranyl sulfate cause the relative rate to approach unity so rapidly means that the absorption coefficient is very high.

In Table II are also given values calculated by means of the following equation.

$$-\mathrm{d}[\mathrm{H_2Ma}]/\mathrm{d}t = \frac{K_1'I_0(1 - 10^{-kCl})}{1 + K_3C}\,[\mathrm{H_2Ma}] + K_2I_0\,10^{-kCl} \tag{2}$$

All terms have the same meaning as in Equation 1. For the values listed in the row marked I, the following constants were used: $K_1'I_0 = 12.9$, $kl = 0.0411$, $K_3 = 1.0$, $K_2 = 0.327$. For the row marked II, $K_1'I_0 = 3.97$, $kl = 0.1$, $K_3 = 0.402$, $K_2I_0 = 0.327$. This equation may be derived by assuming that a complex molecule is formed when an excited uranyl sulfate molecule (or uranyl ion) collides with a malonic acid molecule and that this complex may either decompose into the final products of the reaction (a first order reaction) or may be deactivated by collision with a uranyl sulfate molecule (or uranyl ion). The second term on the right-hand side of the equation has the same significance as the similar term in Equation 1.

Equation 1 agrees with the experimental values satisfactorily. Equation 2 is of such a nature that the rate passes through a maximum as C increases. It may be made to fit the data at lower concentrations as well as Equation 1, but the rate calculated by its use always falls off more rapidly than the experimental value beyond 0.005 M uranyl sulfate if a reasonably good fit is made for the lower part of the curve. We may conclude, therefore, that the assumption that with constant concentration of malonic acid the rate of the catalyzed reaction is proportional to the intensity of the light absorbed by the catalyst does not disagree with the experimental facts.

When attention is turned to the variation of rate with concentration of malonic acid, the question becomes somewhat more complicated. If the rate were independent of concentration of malonic acid, every activated uranyl sulfate molecule (or uranyl ion) would have a chance to react and the low quantum efficiency would be due to the low probability of reaction of the malonic acid after activation by a collision of the second kind. The variation of reaction rate with concentration indicates, however, that part of the absorbed radiation is ineffective in producing activation of malonic acid. This is also borne out by the low value of the quantum efficiency. Likewise complex formation does not offer a simple explanation of the results obtained. The most logical explanation is based on the assumption that uranyl sulfate is activated by absorption of the radiation and that it may lose its energy before encountering a malonic acid molecule. If the deactivation process is a first order reaction and the activation of the malonic acid proportional to the concentration of activated uranyl sulfate molecules and to the concentration of malonic acid, an equation of the following type is obtained

$$\text{Rate} = KC'/(1 + kC) \tag{3}$$

if the light absorbed remains constant. C' is the concentration of malonic acid. This equation does not satisfy the data completely.

One other possibility may be considered. If an activated uranyl sulfate molecule could be deactivated by a collision with another uranyl sulfate molecule or could activate a malonic acid molecule upon collision, the reaction rate should be proportional to the ratio $C'/(C' + C)$, where C' is the concentration of malonic acid and C the concentration of uranyl sulfate. Using average concentrations during each run, relative rates in Table VII may be calculated to be 1.00, 0.70 and 0.30 instead of 1.00, 0.64 and 0.36, respectively. This is a reasonably good check in view of the fact that the water may easily play a part in the deactivation process. It is to be noted that this simple explanation would also account for the slight decrease in rate with high concentrations of uranyl sulfate.

The decomposition of malonic acid in the presence of uranyl sulfate seems, therefore, to be of a type differing from that of oxalic acid. Complex formation seems to offer a reasonable explanation of the results obtained with the latter, although there may still be some doubt as to the quantum efficiencies (the quantum efficiencies in the absence of catalyst would seem to be too low). Most authors are in agreement that addition of uranyl sulfate to oxalic acid increases the quantum efficiency, while addition of uranyl sulfate to malonic acid causes a lowering. While no definite evidence has been obtained for the existence of a light-sensitive complex in solutions containing both uranyl sulfate and malonic acid, such an explanation has not been definitely eliminated. A complex, if present, must either be small in concentration compared to the amount of uranyl sulfate added or be relatively insensitive to the action of radiation.

Summary

1. Malonic acid, both in the presence and absence of uranyl sulfate, decomposes initially to give carbon dioxide and acetic acid.

2. The rate of decomposition in the presence of radiation from the mercury arc increases with addition of uranyl sulfate and approaches a constant value (although there may be a slight decrease at high concentrations).

3. The quantum efficiency of the catalyzed reaction is lower than for the uncatalyzed reaction at the concentrations studied.

4. With constant concentration of uranyl sulfate (0.01 *M*), the rate of decomposition decreases with decrease in concentration of malonic acid. Empirically, the rate is approximately proportional to the cube root of the malonic acid concentration.

5. No good evidence is obtained for the presence of a complex molecule which is light sensitive.

6. Various mechanisms of the reaction have been discussed.

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