alkaline solution of 2 cc. of 0.1% dye in a volume of 50 cc. was very nearly colorless.

4. The lake color remained sufficiently permanent for making determinations until the solution was raised to *P*H 7.4.
5. The presence of ammonium acetate and chloride as buffers was found advantageous for controlling the *P*H of the solution.
6. Ammonium carbonate was found more suitable for decolorizing the excess dye than either ammonium hydroxide or a solution of ammonium carbonate in ammonium hydroxide.

EAST LANSING, MICHIGAN

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

PHOTOCHEMICAL STUDIES. IX. URANYL SULFATE AS SENSITIZER FOR THE PHOTOCHEMICAL DECOMPOSITION OF OXALIC AND MALONIC ACIDS

BY WILLIS CONWAY PIERCE

RECEIVED MAY 1, 1929 PUBLISHED SEPTEMBER 5, 1929

The photochemical decomposition of malonic acid, both in the presence and absence of uranyl salts, has been the subject of a previous study,[1] while the decomposition of oxalic acid has been repeatedly investigated.[2] The results indicate that the mechanisms of the sensitized decompositions of the two acids may be different and the present work was undertaken in order to obtain a more thorough comparison between the two.

I. Temperature Coefficient

There is some discrepancy in the values given for the quantum efficiency of the oxalic acid decomposition but the generally accepted value seems to be one.[3,4] Various workers have reported a temperature coefficient of unity. The quantum efficiency for the decomposition of 0.05 *M* malonic acid with 0.0025 *M* uranyl sulfate was found[1] to be about 0.25, and to be in some degree at least independent of wave length. Büchi[3] attributed the effect of uranyl sulfate to complex formation in the case of oxalic acid. Müller,[5] on the other hand, has attributed the effect to collisions of the second kind between activated uranyl ions and oxalic acid molecules or oxalate ions. A somewhat similar explanation was suggested[1] for the

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[1] See Pierce, Leviton and Noyes, THIS JOURNAL, **51**, 80 (1929), for more complete references.

[2] See Kistiakowsky, "Photochemical Processes," The Chemical Catalog Co., Inc., New York, **1928**, for a review of this work.

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

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

[5] Müller, *Proc. Roy. Soc. London*, **121A**, 313 (1929).

uranyl sulfate–malonic acid reaction, although it was said that complex formation was not definitely ruled out.

It seemed that the temperature coefficient might furnish evidence as to the applicability of the two explanations and this was determined for uranyl sulfate with malonic acid and uranyl sulfate with oxalic acid. A value of one was found for the oxalic acid, confirming the results of Bruner and Kozak[6] and Bacon.[7] The sensitized decomposition of malonic acid showed a temperature coefficient of 1.13 ± 0.02 between 3 and 73°.

Experimental

A quartz mercury arc lamp was mounted vertically and two quartz water jackets surrounding quartz test-tubes were placed parallel to the lamp at a distance of two centimeters. The solutions were placed in the test-tubes and were kept at the desired temperature by a rapid flow of water through the jackets. The system was tested for uniformity by exposing similar samples of a uranyl sulfate–oxalic acid solution in the two vessels and measuring the decomposition by titration with permanganate. Malonic acid solutions were analyzed by titration with carbonate-free sodium hydroxide solution with phenolphthalein indicator. Results are given in Table I.

TABLE I

TEMPERATURE COEFFICIENT.[a] KMnO₄, 0.105 *N*. NaOH, 0.05 *N*

Substances	Temp. interval, °C.	Decomposition cc. $KMnO_4$ hot	cold	Ratio of rate hot/cold	Temp. coef.
10 cc. 0.2 *M* $H_2C_2O_4$; 0.002 *M* UO_2SO_4	3–63	9.94	8.55	1.08	1.01+
	3–63	10.73	10.98	0.98	1.00
		NaOH, cc.			
10 cc. 0.1 *M* $H_2C_3H_2O_4$; 0.0025 *M* UO_2SO_4	3–73	11.55	5.00	2.31	1.13−
	3–73	11.25	4.70	2.39	1.13+
	3–73	13.60	5.74	2.37	1.13
	3–53	11.10	5.20	1.95	1.14+

[a] By "temperature coefficient" is meant the ratio of the rates, $R_{t+10°}/R_t$.

These results confirm a large number of previous runs in which but a single sample was exposed.

II. Absorption Spectra

The absorption coefficients of uranyl salts are greatly enhanced by the presence of organic acids. Henri and Landau[8] first described this for oxalic acid and uranyl sulfate and their work was cited by Büchi as evidence for complex formation. It was stated in the previous paper that no such effect was found with malonic acid, but a further investigation at higher

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[6] Bruner and Kozak, *Z. Elektrochem.*, **17**, 355 (1911).

[7] Bacon, *The Philip. J. of Sci.*, **5**, 281 (1910).

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

frequencies (using more dilute solutions) showed that in the range 220 mμ to 320 mμ the absorption coefficients are increased by the presence of malonic acid. The effect is not so marked at longer wave lengths. Ghosh and Mitra[9] assumed that this enhancing effect is due to the formation of a complex between the uranyl salt and the organic acid and used the absorption coefficients to calculate the degree of formation. Both oxalic and malonic acids were investigated by them. They based their calculations on the assumptions that (1) one molecule of the organic acid unites with one molecule of the uranyl salt to form a molecular complex, (2) the mass law applies to this combination and (3) the complex molecule has a definite absorption coefficient for each wave length. They found the equilibrium constants

$$\left(K = \frac{[\text{complex}]}{[\text{uranyl salt}]\,[\text{organic acid}]}\right)$$

$K = 115$ for oxalic acid–uranyl sulfate complex and $K = 80$ for malonic acid–uranyl sulfate complex. According to these values oxalic and malonic acids form complexes of about the same degree of stability but the absorption of the oxalic acid complex is much greater than that of the malonic acid complex.[10]

The work of Müller,[5] Jette and West,[11] and West, Müller and Jette[12] suggested that the increase in the absorption might be due to quenching the fluorescence of the uranyl ion. They found that chloride ion was effective in quenching the fluorescence and that sulfate ion had relatively little effect. The absorption coefficients were determined for uranyl sulfate with these added ions. Neither had an appreciable effect in dilute solution but 0.001 *M* uranyl sulfate in saturated potassium chloride or potassium sulfate showed practically the same absorption coefficients as when dissolved in 0.01 *M* oxalic acid. From these results and the fact that Beer's law is obeyed for dilute solutions of uranyl salts it was concluded that the quenching of the fluorescence is probably not the reason for the enhancing of the absorption. The peculiar enhancing by saturated salt solutions may be due to the formation of very unstable complexes but no attempt was made to investigate these.

III. Effect of Concentration on the Rate of Reaction

(a) **Uranyl Sulfate.**—It was stated in the previous paper that the rate of reaction varied with the concentration of uranyl sulfate when it was

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[9] Ghosh and Mitra, *J. Indian Chem. Soc.*, **4**, 353 (1927).

[10] Absorption coefficients were determined for oxalic and malonic acids and for their solutions with uranyl sulfate before noting the above work. The results were in qualitative agreement with the work of Ghosh, although the difference in the enhancing due to oxalic and malonic acids was not so great as that found by Ghosh.

[11] Jette and West, *Proc. Roy. Soc. London*, **121A**, 300 (1928).

[12] West, Müller and Jette, *ibid.*, **121A**, 294 (1928).

less than 0.0025 *M* and was independent of concentration in the range 0.0025 to 0.01 *M*. This was for reactions carried out in vessels exposing a layer of solution one to two centimeters in depth. All of the previous work was done with only one exposure at a time and was open to error in accidental variation in the light intensity. A new series of experiments was carried out with all the samples of varying concentration lighted simultaneously on a rotating motor-driven turntable. The results are listed in Table II. They are in agreement with the previous results.

TABLE II

VARIATION OF RATE WITH CONCENTRATION OF URANYL SULFATE

10-cc. samples lighted in open porcelain crucibles. Depth of liquid, 1.5 cm. Malonic acid, 0.05 *M*. NaOH, 0.0528 *N*.

Concn. UO_2SO_4	Amt. decomp. (cc. NaOH) I	II	Relative rate 2.72 = 1	8.15 = 1
0.0000	0.50	1.71	0.18	0.21
.0005	1.75	5.05	0.64	0.62
.0010	2.29	6.03	0.84	0.74
.0015	2.38	6.76	0.88	0.83
.0025	2.75	7.58	1.01	0.93
.0050	2.63	8.39	0.97	1.03
.0075	2.86	8.47	1.05	1.04
.0100	2.64	8.15	0.97	1.00

(**b**) **Malonic Acid.**—It has previously been shown that with 0.01 *M* uranyl sulfate the rate varied with the concentration of malonic acid. The effect is most marked at small concentrations of acid. The importance of this led to a reinvestigation, using a greater variety of mixtures. All samples were lighted simultaneously on the rotating apparatus, thus eliminating errors due to fluctuations in the light intensity. The total reaction had to be kept small in order to prevent complete decomposition of the samples having small amounts of malonic acid, and on this account the experimental error was quite large. Averages taken from a large number of determinations gave sufficient accuracy to determine the trend of the rate curve. Results of two typical runs are given in Table III.

TABLE III

VARIATION IN RATE WITH CONCENTRATION OF MALONIC ACID

Uranyl sulfate, 0.0116 *M*. 20-cc. samples used. NaOH, 0.0528 *N*

	2.5-Hour run				5.8-Hour run			
Init. concn. malonic acid	0.0046	0.0092	0.023	0.046	0.0092	0.023	0.046	0.092
Molar ratio = x	0.4	0.8	2.0	4.0	0.8	2.0	4.0	8.0
Amt. dec., cc. of NaOH	1.30	1.59	1.95	2.60	2.97	4.91	5.58	6.18
Rel. rate, $x = 8$, for unity	0.45	0.55	0.67	0.90	0.48	0.79	0.90	1.00
Av. molar ratio, $\bar{x}$	0.25	0.61	1.8	4.0–	0.4	1.5	4.0–	8.0–

The two series of runs were calculated to the same relative rate of unity for samples having a molar ratio of 8. Since the concentration changed during a run, an average value of x (molar ratio) was calculated and used as the effective molar ratio. This does not accurately represent the effective concentrations during a decomposition but it may be taken as a first approximation.

IV. Discussion of Results

Some points of difference are noted in the catalyzed decompositions of oxalic and malonic acids. For example, the temperature coefficient of the former is one while that of the latter is 1.13. The quantum efficiency of the former is given as one, but for the latter a value of about 0.25 was found. On the other hand, many points of similarity lead to the conclusion that the function of the uranyl sulfate is the same in both cases. It seems that both reactions may be satisfactorily explained by the assumptions of Büchi that a light-sensitive complex is formed by the uranyl ion and the organic acid, and that decomposition is caused only by the light absorbed by this complex. There is, however, some evidence for the alternative theory that the uranyl ion transfers energy to the acid molecule by collisions of the second kind. Indications of complex formation to be found are: (1) The conductivity of uranyl salts was shown by Dittrich[13] to be lowered by the addition of sodium oxalate.

(2) The quantitative work of Ghosh and Mitra on the absorption spectra seems to point to complex formation.

(3) The variation in rate with the concentration of acid may be in agreement with the "complex" theory. Büchi showed that for oxalic acid the rate is nearly constant when the molar ratio is greater than one (acid in excess). This is difficult to explain by collisions of the second kind unless the activated uranyl ions have a very long life and may be deactivated only by collision with oxalic acid molecules. It is, however, in harmony with the "complex" theory if the complex has such large absorption coefficients that practically all of the effective light is absorbed by it, and if the complex is so stable that when a molar ratio of unity is reached practically all of the uranyl ions are combined. Both of these assumptions are necessary to account for a quantum yield of unity, as found by Büchi.

These assumptions, however, are not in agreement with the values of Ghosh[9] for the stability of the complex and its absorptive power. Büchi used 0.0167 M uranyl sulfate solutions with equimolar oxalic acid. Ghosh found an equilibrium constant of 80 for this reaction. This value leads to a calculated concentration of complex of 0.006 M for the above solution. The relative absorption for a given frequency is given by the relation

$$\text{Fraction of light absorbed by complex} = \frac{k_1c_1}{k_1c_1 + k_2c_2}$$

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[13] Dittrich, *Z. physik. Chem.*, **29**, 449 (1899).

where k_1 and k_2 are absorption coefficients of complex and uranyl ion, respectively, and c_1 and c_2 are their concentrations. In order for the complex to absorb most of the light its absorption coefficient must be very much greater than those of the uranyl ion if the relative concentrations are as given by the calculation. It seems then that (1) the complex may be more stable than postulated by Ghosh, (2) it may have larger absorption coefficients, or (3) energy absorbed by the uranyl ions may be transferred to the complex by collisions of the second kind of very high efficiency.

The case of malonic acid is much the same. The increase in rate beyond a molar ratio of 1 is very much less than when the uranyl sulfate is in excess. The reaction may be satisfactorily interpreted as due to the absorption of light by the complex and decomposition of the activated complex. The steady rise in rate with increasing acid concentration may be due to the formation of more of the complex, thus increasing the fraction of the light absorbed by the complex.

This interpretation does not conflict with the observation that in 0.05 *M* malonic acid solutions the rate is independent of the uranyl salt concentration in the range 0.0025 to 0.01 *M*. At such concentrations absorption of the effective light is undoubtedly nearly complete even in very shallow layers, and increase in the complex concentration should not cause an increase in rate. Further, increase in the concentration of uranyl ion decreases the molar ratio so that the fraction of the uranyl ion converted to complex becomes smaller as its total concentration is increased, and less of the light is available for the reaction. A calculation of the fraction converted may be made using the equilibrium constant of 115 as determined by Ghosh. At initial concentrations of UO_2SO_4 = 0.0025 and malonic acid = 0.05 *M* the concentration of complex is 0.00217 *M*, or 86.7% of the ion has reacted. For 0.01 *M* UO_2SO_4 and 0.05 *M* malonic acid the complex concentration is 0.00827 *M*, corresponding to 82.7% reaction. Since the absorption coefficients of the complex are higher than those of the uranyl ion, the fraction of the light absorbed by the complex does not change greatly over this range of concentration of uranyl ion.

(4) The temperature coefficient of unity may be in harmony with either mechanism for oxalic acid. If the reaction is a zero order decomposition of a complex, it appears that the activation of any molecule may lead to decomposition, and that thermal activation is not necessary. It would seem that temperature changes have little effect on the stability of the complex since the reaction rate is independent of temperature. If, on the other hand, the reaction is brought about by collisions of the second kind, all absorbed quanta must be utilized in activating oxalic acid molecules and rise in temperature should cause no change in rate.

It is significant that the temperature coefficient of the malonic acid reaction is so much larger, but this fact as well as the quantum efficiency may agree equally well with either explanation.

Collisions of the second kind do not seem to offer an adequate explanation of the enhancing of absorption when organic acids are added to uranyl sulfate solution. On the other hand, complex formation does not seem to explain the observation of Müller[5] that addition of certain ions to a uranyl sulfate–oxalic acid solution lowers the rate of reaction. He found that the order of effectiveness of chloride, bromide and thiocyanate ions is the same as their order of effectiveness in quenching the fluorescence of uranyl ions. Both effects are ascribed to the ability of the added ions to deactivate the uranyl ions on collision. If such a deactivation occurs, the effectiveness of added ions in reducing the rate of oxalic acid decomposition should depend (a) on the effectiveness of transfer of energy from the uranyl ion to retarder and to reactant, and (b) the relative number of collisions of each with the activated uranyl ions. These assumptions have been used to calculate the rate of decomposition of 0.1 *M* oxalic acid in the presence of various retarders. The experimental results are those given by Müller.[5] Results are summarized in Table IV. The assumed effectiveness of the deactivation per collision with a retarding ion is: chloride ion, 0.228; bromide ion, 0.5; thiocyanate ion, 1.0. It is significant that the inhibitor having the greatest effect has an efficiency of deactivation of unity.

Table IV

Inhibiting Effect of Added Ions

Concn. of added ion	Calcd. rate Cl	Obs. rate Cl	Calcd. rate Br	Obs. rate Br	Calcd. rate SCN	Obs. rate SCN
0.02	26.9	27.1	25.6	26.2	23.3	23.0
.05	25.8	26.1	23.3	24.2	18.7	18.5
.10	(24.8)	24.8	21.0	22.3	14.0	13.8
.20	23.7	24.2	18.7	19.4	9.3	8.6

The excellent agreement obtained lends support to this theory.

Each theory then may account for many of the observed facts, and it seems that further work is needed in order to establish either one. A third possibility is that the reaction is brought about by both complex formation and collisions of the second kind.

V. Summary

1. The temperature coefficient is 1.13 + 0.02 for the photolysis of malonic acid in presence of uranyl sulfate. It is unity for oxalic acid–uranyl sulfate, as reported by previous workers.

2. The rate of the reaction varies with the concentration of uranyl sulfate and approaches a constant value. The rate varies with the concentration of malonic acid. This effect is greatest when the molar ratio of malonic acid to uranyl sulfate is less than unity. At ratios greater than unity the change in rate with concentration is small.

3. The oxalic and malonic acid reactions seem to be similar although they show a marked difference in their temperature coefficients and quantum efficiencies.

4. Two mechanisms are discussed. The reaction may be due to the decomposition of an intermediate uranyl ion–acid complex, or it may be explained by collisions of the second kind between activated uranyl ions and acid molecules.

CHICAGO, ILLINOIS

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

THE HEAT CAPACITY OF TOLUENE FROM 14°K. TO 298°K. THE ENTROPY AND THE FREE ENERGY OF FORMATION

BY KENNETH K. KELLEY[1]

RECEIVED MAY 6, 1929 PUBLISHED SEPTEMBER 5, 1929

Very few low temperature thermal measurements on aromatic hydrocarbons have been made. The only true specific heats which have been published are those of Nernst[2] for benzene but even these data are very scanty and do not agree well among themselves.

This paper presents specific heat, heat of fusion and temperature of fusion data for toluene. The specific heat measurements were carried down to 14°K. The methods and apparatus and the accuracy of measurement have been discussed elsewhere.[3]

One change in the apparatus was made before starting this work. Due to an unfortunate explosion the portable hydrogen liquefier, previously used, was demolished. A new liquefier, similar to that described by Latimer and Greensfelder,[4] was built in as a permanent unit. Both of these liquefiers were designed by Mr. G. F. Nelson of this Laboratory and built under his supervision.

Material.—The toluene was the best product of the Eastman Kodak Company (sulfur free). Treatment of a sample with concd. sulfuric acid gave no coloration in ten minutes. The material was dried for several days with fused calcium chloride, decanted off, and carefully fractionated three times. The middle portion used had a volume of 200 cc. and a boiling range of 0.03°. The density, d_4^0, 0.88456, compares favorably with the Leiden measurement,[5] d_4^0, 0.88445, and with that of Biron,[6] d_4^0, 0.88450. The fusion curves indicated exceptional purity.

The Measurements.—The specific heat results are given in Table I and shown graphically in Figure 1. No abnormal behavior was noted in either the crystals or liquid.

[1] National Research Fellow in Chemistry.

[2] Nernst, *Ann. Physik*, (4) **36**, 395 (1911).

[3] Kelley, THIS JOURNAL, **51**, 180 (1929).

[4] Latimer and Greensfelder, *ibid.*, **50**, 2209 (1928).

[5] *Comm. Phys. Lab. Univ. Leiden*, No. 157.

[6] Biron, *Chem. Zentr.*, I, 1910 (1913).