

TABLE IV

ANALYSIS OF REACTION PRODUCTS

Experiment	Calcd. for PCl ₃ : P, 22.58.		Calcd. for PSCl ₃ : P, 18.31; S, 18.88	
	P found, %	S found, %	PSCl ₃ (from S), %	
6	22.47	0.61	3.23	
7	21.19	6.19	32.74	
8	19.81	12.68	67.16	
9	18.53	19.14	100.0	
14	18.69	18.29	96.87	
15	18.62	18.72	99.15	

The mechanism of the catalysis may well be explained by the intermediate compound theory in which the polysulfide is the active agent. Thus any basic substance with which sulfur easily reacts to give addition compounds would probably serve as a condensing agent for the reaction. For example, it has been observed that free caustic soda will catalyze the reaction. It was customary to clean the autoclave with hot caustic soda solution after each experimental run, and if the alkali were not thoroughly removed, reaction resulted in those experiments where no catalyst had been added.

Summary

Phosphorus trichloride and sulfur do not react at atmospheric pressure and at the boiling point of the solution. At 150° a slow, partial reaction to form phosphorus thiochloride takes place.

Small amounts of alkali metal sulfides, alkaline earth metal sulfides or substances of like character which add on sulfur catalyze the reaction between phosphorus trichloride and sulfur so that conversion to phosphorus thiochloride is complete at 150° within a short period of time.

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THE PHOTOCHEMICAL DECOMPOSITION OF ORGANIC ACIDS¹

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Quantitative studies have been made of the photochemical decomposition of aqueous solutions of oxalic,² formic,³ lactic⁴ and malonic⁵ acids. Oxalic acid absorbs light of wave lengths below 365 mμ, decomposing to formic acid and carbon dioxide. The quantum yield is small. Formic acid de-

¹ A report of part of this work was presented at the Fall Meeting of the American Chemical Society at Minneapolis, 1929.

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

³ Allmand and Reeve, *ibid.*, 129, 2852 (1926).

⁴ Burns, *THIS JOURNAL*, 51, 3165 (1929).

⁵ Pierce, Leviton and Noyes, *ibid.*, 51, 80 (1929).

composes in two ways, giving either carbon dioxide and hydrogen or carbon monoxide and water. The quantum yield is near unity for light of wave length near $300\text{ m}\mu$ and rises for light of shorter wave length. Lactic acid gives carbon dioxide as the chief gaseous product. The quantum efficiency is about 0.65 in dilute solution. According to previous work in this Laboratory⁵ malonic acid absorbs light in the ultraviolet region, decomposing to give carbon dioxide and acetic acid. The quantum efficiency was estimated as 0.75 ± 0.25 for 0.05 m solutions. The decomposition was thought to be due to undissociated molecules since addition of strong acids did not affect the light sensitivity. The reaction, like that of oxalic acid, is sensitized to light of longer wave lengths by the addition of uranyl salts, but the quantum efficiency of the sensitized reaction is less than for the unsensitized.

In the present work a more thorough study of the mechanism of the photochemical decomposition of organic acids is undertaken. Because of the simplicity of its decomposition malonic acid was first investigated.

Change in Rate with Concentration.—Duplicate samples of varying concentration were lighted simultaneously on a rotating stand in order to insure uniformity of illumination. The full light of a vacuum type mercury arc lamp was used. The amount of decomposition was determined by titration with sodium hydroxide, unlighted samples being used as controls for each determination. The experimental error was large since the total decomposition had to be kept low in order to prevent complete decomposition of the more dilute samples. A summary of the results is given in Table I. The average concentration was taken as the arithmetical mean of the initial and final concentrations. The variation in rate is much less than the variation in concentration, but it is possible that this is due to decomposition of acetic acid in the more dilute samples, thus making the apparent rate larger than the true value.

TABLE I

Run	VARIATION IN RATE WITH CONCENTRATION				
	Initial concn., <i>m</i>	Decompn., cc. NaOH	Per cent. decompn.	Av. ratio concn.	Ratio of rates
1	0.1	4.65	22	13	3.7
	.01	1.27	64		
2	.1	1.92	9	12	3.6
	.01	0.54	39		
3	.1	2.43	11	13	2.5
	.01	0.97	58		

Variation in Absorption with Concentration.—It was thought that the small variation in rate shown in Table I might be due to variation in the amount of light absorbed by the solutions. In order to test this the total absorption of light was determined for the concentrations used in the

experiments. A parallel beam of light was passed through a layer of solution and the intensity measured by a sensitive thermopile. Blank determinations were made with the solution replaced by a vessel filled with distilled water. The fraction of the total light absorbed by solutions of various concentration is shown in Fig. 1. At small concentrations the fraction of the light absorbed seems to vary as the concentration. Because of the inherent large errors in this and the preceding experiment no conclusions may be safely drawn as to the order of the reaction except that it is not higher than first order.

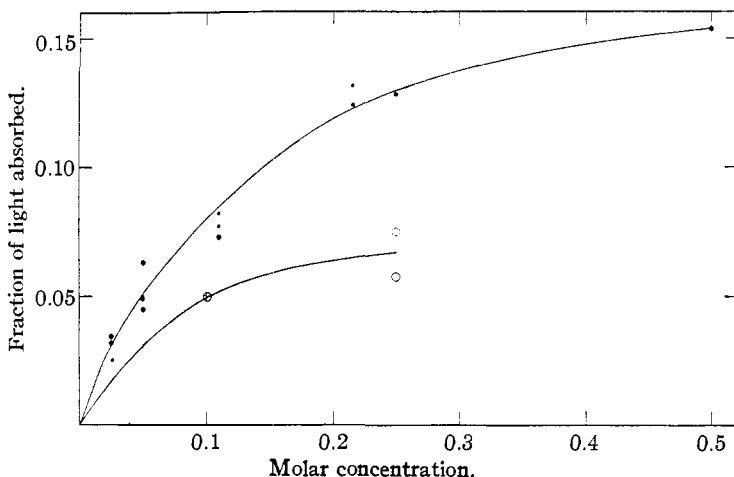
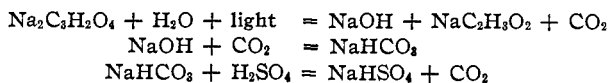


Fig. 1.—Fraction of light from mercury arc lamp absorbed by malonic acid (upper) and sodium malonate solutions.

Effect of Salt Formation.—A comparison was made of the relative rates of decomposition of malonic acid and sodium malonate, 0.1 *m* samples of each being lighted simultaneously. Hydrolysis of the salt solution was prevented by the addition of a slight excess of sodium hydroxide. The amount of decomposition of the salt solution was determined by adding excess sulfuric acid, boiling off the evolved carbon dioxide and titrating the remaining acid with standard sodium hydroxide. An unlighted sample was used as a control test in each experiment. The procedure was based on the following reactions



That this is the course of the reaction was proved by testing for acetate after lighting and by the absence of gas evolution from a lighted sample of the salt solution. The relative rate of decomposition of malonic acid was found to be about five times that of sodium malonate.

Absorption Spectra.—The total absorption of sodium malonate solutions was determined for various concentrations. The results are shown in the lower curve of Fig. 1. Since the absorption is about half that of the malonic acid and the rate of decomposition about one-fifth, the quantum efficiency is estimated to be about one-half that of malonic acid.

The molar absorption coefficients⁶ of acid and salt were determined by the rotating sector method with a Hilger E2 quartz spectrograph. The

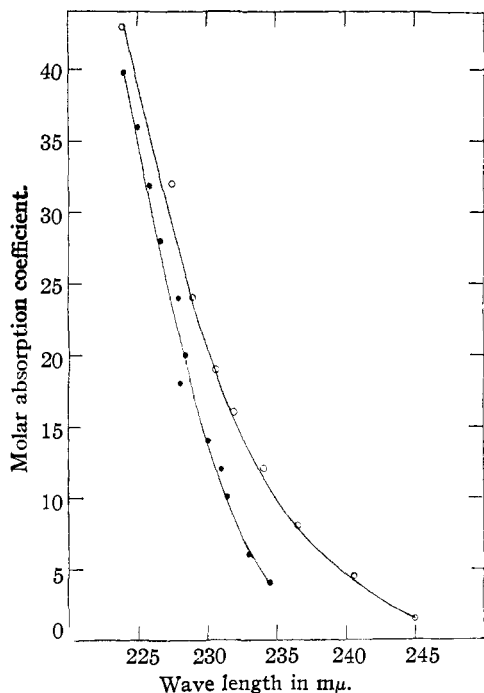


Fig. 2.—Molar absorption coefficients of malonic acid (upper) and sodium malonate.

values are plotted in Fig. 2 for various wave lengths. In all measurable regions the acid shows a much higher absorption than the salt. The results are in agreement with the measurements of Bielecki and Henri⁷ for malonic acid and with the observation of Wright⁸ that salt formation lowers the absorption of light.

Temperature Coefficient.—

The temperature coefficient was determined by simultaneous lighting of two samples, one at 3° and the other at 70°. Two quartz test-tubes, surrounded by quartz water jackets, were mounted in optically equivalent positions near the lamp and the desired temperatures maintained by a rapid flow of water through the jackets. The "ten degree" temperature coefficient was found to be 1.07 for the range investigated. This is not due to a change in absorption, for hot and cold samples were found to absorb the same amount of light.

Acetic and Propionic Acids.—Aqueous solutions of these acids were lighted in an enclosed apparatus and the evolved gases pumped off and analyzed. For acetic acid the main products were equivalent quantities of

⁶ By "molar absorption coefficient" is meant the constant of the Beer's law equation $\log I_0/I = kcd$

in which k is the constant, c is the molar concentration and d is the thickness in centimeters.

⁷ Bielecki and Henri, *Ber.*, **45**, 2819 (1912).

⁸ Wright, *J. Chem. Soc.*, **103**, 528 (1913).

carbon dioxide and methane with small quantities of carbon monoxide and unsaturated hydrocarbons. The chief products for propionic acid were carbon dioxide and ethane in equivalent quantities. The hydrocarbons were identified by explosion with oxygen.

Discussion and Conclusions

The decomposition of malonic acid after activation by light seems to be independent of concentration since the variation in rate with concentration is less than the variation in concentration. The quantum efficiency of the reaction may be recalculated on the basis of the present absorption measurements, giving a value of $0.5 \approx 0.25$ molecule per quantum for the whole light of the mercury arc lamp. No attempt has been made to employ monochromatic light because of the low intensity of the short wave lines of the mercury spectrum.

Qualitative confirmation of the low quantum efficiency may be obtained from the temperature coefficient. According to Tolman's theory of the temperature coefficient only molecules having an energy content above the average may decompose on absorption of light in reactions having a temperature coefficient larger than unity. Calculations based on the present value of 1.07 for the temperature coefficient indicate that an energy increment of about 600 calories per mole is necessary for the molecules that may decompose. The probability that a molecule will have this amount of excess energy is about 0.4, a value in agreement with the observed quantum efficiency.

The results with sodium malonate show that the decomposition is not due primarily to the ions present, confirming the previous findings with respect to the addition of strong acids. However, it seems that the course of the reaction is the same for the salt and acid since the same products are obtained, namely, carbon dioxide and acetic acid or acetate ion. The results with acetic and propionic acids, when considered with the above, lead to the conclusion that the primary process in the decomposition of organic acids is a splitting out of carbon dioxide, leaving the remainder of the molecule unchanged. No definite reason may be given for the smaller absorption and the decreased quantum efficiency for the salt, although the similarity in the processes suggests that light is absorbed by the O-H valence electrons of the acid and that in the ion these are more tightly held, requiring more energy for activation.

No attempt has been made to determine the quantum efficiency for acetic and propionic acids, but a qualitative comparison of the velocity of decomposition with that of malonic acid shows about the same rates. Since the absorption also lies in the same region, the quantum efficiency is probably of the same order.

For an organic acid showing a low quantum efficiency, such as oxalic,

the absorption is over a much wider region. Allmand and Reeve³ found quantum efficiencies ranging from 0.01 at 265 $m\mu$ to 0.00095 at 365 $m\mu$. Possibly only the light absorbed by the carboxyl group causes decomposition, and apparently this lies in the region below 250 $m\mu$.

Summary

A further study is made of the photochemical decomposition of malonic acid and the results obtained are applied to the general process of photochemical decomposition of carboxyl groups. The effective light in this process seems to lie in the region 200–250 $m\mu$. Decomposition gives as products carbon dioxide and a hydrocarbon residue. Photochemical decarboxylations are characterized by low temperature coefficient, quantum efficiency near unity, low absorption of light. Presence of other absorbing groups in the molecule may modify these characteristics.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS]

GLACIAL ACETIC ACID AS A SOLVENT FOR THE ELECTRODEPOSITION OF METALS.^{1,2} AN X-RAY DIFFRACTION STUDY OF THE STRUCTURE OF DEPOSITS OF ARSENIC, ANTIMONY AND BISMUTH

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A considerable number of investigations have demonstrated that a variety of solvents may be employed for the electrodeposition of metals,^{2c} and in some instances these studies have shown that certain non-aqueous solvents may be employed with distinct advantage over water. A survey of solvents used for this purpose reveals that they are all either basic or amphiprotic in nature and that no definitely acidic solvent has yet been investigated. However, most compounds of such elements as arsenic, antimony, bismuth and stannic tin undergo considerable solvolysis in basic solvents and dissolve only in the presence of acids. The striking solubility of the chlorides of these elements in glacial acetic acid with the apparent non-formation, at least of insoluble, solvo-basic products, indicated immediately that it might be of considerable theoretical interest to study the discharge of these metallic cations from glacial acetic acid.

Glacial acetic acid has been shown to be an excellent ionizing medium

¹ This paper was presented at the Buffalo meeting of the American Chemical Society, September, 1931.

² For earlier papers of this series see (a) Yntema and Audrieth, *THIS JOURNAL*, **52**, 2693 (1930); (b) Audrieth and Yntema, *J. Phys. Chem.*, **34**, 1903 (1930); (c) Audrieth and Nelson, *Chem. Reviews*, **8**, 335 (1931); (d) Audrieth, Jukkola, Meints and Hopkins, *THIS JOURNAL*, **53**, 1805 (1931).