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

PHOTOCHEMICAL STUDIES. I. THE PHOTOCHEMICAL DECOMPOSITION OF SOLID OXALIC ACID[1]

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Much work has been done on the photochemical decomposition of solutions of oxalic acid,[2] but very little work has appeared on the decomposition of the solid.

Berthelot and Gaudechon[3] studied the photochemical decomposition of anhydrous oxalic acid and reported that it was decomposed by ultraviolet light of wave length shorter than 300$\mu\mu$. Analysis of their products showed 87% of carbon dioxide, 9.5% of carbon monoxide and 3.5% of hydrogen together with traces of formic acid. The temperature of the acid attained 95°, probably due to the proximity of the mercury arc lamp, which was placed at a distance of only 2 cm.

In the present article it is desired to present a study of the rate of photochemical decomposition of solid oxalic acid, together with a rough determination of the most effective wave length for the decomposition. We have shown that the photochemical decomposition is markedly increased by the presence of water and that the speed of decomposition increases with increasing frequency of the radiation employed.

Experimental Procedure

Two sources of ultraviolet light were used: an ordinary carbon arc lamp (in one case the electrodes were soaked in a solution of cobalt, uranium and molybdenum salts), and a mercury arc lamp. The latter was made of Pyrex glass and fitted with a side arm on the end of which could be cemented either a fluorite or a quartz window. The carbon arc lamp gives little ultraviolet radiation below 300$\mu\mu$ and practically none below 250$\mu\mu$. When the electrodes were soaked in the salt solutions this limit was extended to approximately 220$\mu\mu$. Quartz transmits as far as 185$\mu\mu$ and fluorite to approximately 100$\mu\mu$. When the mercury arc lamp was used the window of the lamp was placed in direct contact with the window of the reaction chamber so that the thickness of air traversed by the radiation was negligible. The length of the side arm on the mercury arc lamp was

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[1] The material presented in this article formed part of a thesis presented by A. B. Kouperman to the Ogden Graduate School of Science of the University of Chicago in partial fulfilment of the requirements for the degree of Master of Science. This article is preliminary in nature, but it was deemed wise to publish the results obtained since it may be impossible to continue the work in the near future.

[2] See, for example, Bongiovanni, *Gazz. chim. ital.*, **46**, 127 (1916). Mathews and Dewey, *J. Phys. Chem.*, **17**, 211 (1913). Fay, *Am. Chem. J.*, **18**, 269 (1896). Bruner and Kozak, *Z. Elektrochem.*, **17**, 354 (1911).

[3] Berthelot and Gaudechon, *Compt. rend.*, **158**, 1791 (1914).

sufficient to prevent appreciable heating of the solid. The greatest elevation of temperature noted was 3°.

The pressure changes were measured either by means of a MacLeod gage or by an ordinary manometer, depending on the magnitude of the pressure. The MacLeod gage was so constructed as to indicate pressures up to 15 mm.

The apparatus was first evacuated by means of an oil pump and then further evacuated to a pressure of about 0.005 mm. by means of a Toepler pump. The rates of decomposition of the following substances were studied: (1) anhydrous oxalic acid; (2) oxalic acid dihydrate; (3) a saturated solution in contact with an excess of the solid; (4) formic acid.

Results

By the use of the various sources of ultraviolet light, the effects of the following approximate ranges of wave lengths could be studied: $> 250\mu\mu$, $> 220\mu\mu$, $> 185\mu\mu$, $> 100\mu\mu$.

Summary of Results

Substance decomposed	Period of induction Minutes	Total pressure change in period of induction Mm. × 10^{-2}	$\frac{dp}{dt}$ after induction period (constant) Mm. × 10^{-2}	Wave length $\mu\mu$ >
Saturated solution	15	220	3.5	185
$H_2C_2O_4.2H_2O$	65	300	15.0	185
$H_2C_2O_4$	...	...	...	250
	Indefinite	...	0.09[a]	220
	Indefinite	...	0.08[a]	185
	80	36.4	1.4	100
	140	10.8	0.92	100
	180	10.4	1.1	100
HCOOH	Small	...	8.3	185

[a] These two results should not be directly compared, since the carbon arc lamp was used in one case and the mercury arc lamp in the other. The current flowing through the mercury arc lamp was very nearly constant in all cases.

Discussion of Results

The rate of decomposition evidently depends on the amount of water present. In the case of the solution a large portion of the radiant energy was undoubtedly transmitted, so that this rate is not directly comparable with the other. It is significant that in spite of this fact the rate is greater than for the anhydrous solid. Since water vapor may be one of the products of the decomposition, the reaction is autocatalytic. The induction period may be explained in this manner or it may be explained in either of two other ways. (1) It may be due to the slow formation of formic acid, the latter being rapidly decomposed. In this case the rate of reaction would not reach a maximum until the rate of formation of the formic acid had become constant. This explanation seems hardly acceptable, although formic acid is evidently rapidly decomposed by the radiation from the mercury arc lamp. (2) It may be due to the slow rate of diffusion out of the solid and away from the surface. This factor would not be important if only the surface molecules were decomposed. If molecules in the interior of the crystals were decomposed the gases formed would only slowly diffuse out and the rate of reaction as measured by the pressure would become constant only when a mobile equilibrium was established, the number of molecules of gas diffusing out being then equal to the number formed by the action of the radiation. The effect of higher frequencies in causing more rapid decomposition may be partially explained in this way, since the energy, beyond that actually necessary to decompose the molecules, might be converted into kinetic energy causing the products of the decomposition to diffuse out more rapidly. This would be analogous to the photo-electric effect in which the speed of the electrons emitted is a function of the frequency of the incident radiant energy. In solution this increase of reaction rate with increase in frequency would be much less, if present at all.

The exact role played by water is difficult to ascertain. It may be analogous to the effect of nitrogen dioxide on the decomposition of nitrogen pentoxide in the experiments of Daniels and Johnston.[4]

We carried out a rough determination of the temperature coefficient of thermal decomposition of oxalic acid. Using the formula of Perrin[5] $d\ln k/dT = Nh\nu/RT^2$, the wave length calculated was much greater than that found experimentally as necessary for the decomposition of the solid. It did agree, within the experimental error, with that necessary to decompose the solution of oxalic acid.

After the induction period the rate of decomposition is constant and the amount of acid decomposed is, therefore, proportional to the amount of radiant energy incident on the solid.

Summary

1. Anhydrous oxalic acid is decomposed by ultraviolet light of wave length shorter than 250$\mu\mu$. The rate is greater for shorter wave lengths.

2. The reaction rate is much increased by the presence of water.

3. There is a long induction period. Possible explanations of this are discussed.

4. After the induction period the rate of reaction is constant.

5. The wave length necessary to decompose the solid acid does not agree with that calculated from Perrin's formula based on a rough determination of the temperature coefficient of the rate of thermal decomposition.

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[4] Daniels and Johnston, THIS JOURNAL, **43**, 72 (1921).

[5] Perrin, *Ann. phys.*, **11**, 5 (1919).