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The Photochemical Decomposition of Rotenone

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Rotenone has been reported to undergo decomposition when solutions in organic solvents are allowed to stand.^{1,2} The rate of this decomposition varies with the solvent used. Among the various solvents studied, Jones¹ found that decomposition is most rapid in pyridine solution, while benzene and alcohol were found to give the least decomposition. These results are based on observations of the rate of change of color in solutions, although this change was also accompanied by a change in optical rotation and a loss in toxicity to fish and insects. Since the ultraviolet absorption spectrum of rotenone has been carefully studied,^{3,4,5} we have applied the spectroscopic method to its decomposition.

In their study of the loss of toxicity upon exposure to light, Jones and his co-workers⁶ found that the photochemical decomposition of dry rotenone does not take place in the absence of oxygen. Jones and Haller² also found that the change which takes place in pyridine solution is accelerated by exposure to air, and is not influenced by differences in light intensity. The above findings seem to indicate that light alone does not effect a photo-decomposition of rotenone. We have now found that solutions of rotenone in alcohol undergo photo-chemical decomposition in the absence of oxygen.

Photochemical Decomposition of Rotenone in Ethyl Alcohol.—The rotenone and the ethyl alcohol used were purified in the manner previously reported.⁵ The solution of rotenone in ethyl alcohol (6.67×10^{-5} molar) was divided into approximately equal portions. One portion was saturated with oxygen taken directly from the tank. The other portion was saturated with carbon dioxide prepared by the action of hydrochloric acid on limestone, the gas being passed through sodium bicarbonate solution and a calcium sulfate drying tube. To prevent possible evaporation, both gases were saturated with ethyl alcohol before bubbling through the rotenone solutions. Each solution was then saturated with the respective gas by bubbling through at a rate of two bubbles per second for a period of twenty minutes. The solutions were next transferred to 20-cm. quartz absorption tubes, the outlet be-

ing tightly covered with tin foil, and then exposed to direct sunlight. At intervals of every three days during the period of exposure, the solutions were again saturated with the respective gases. Two solutions similarly treated were kept in the dark room as controls. The absorption spectra of the four solutions were examined immediately after the solutions were prepared and saturated with the respective gases and at intervals of five, ten and twenty days, thereafter, appropriate portions of the solution having been removed for the absorption measurement. The technique followed was that previously reported.⁵

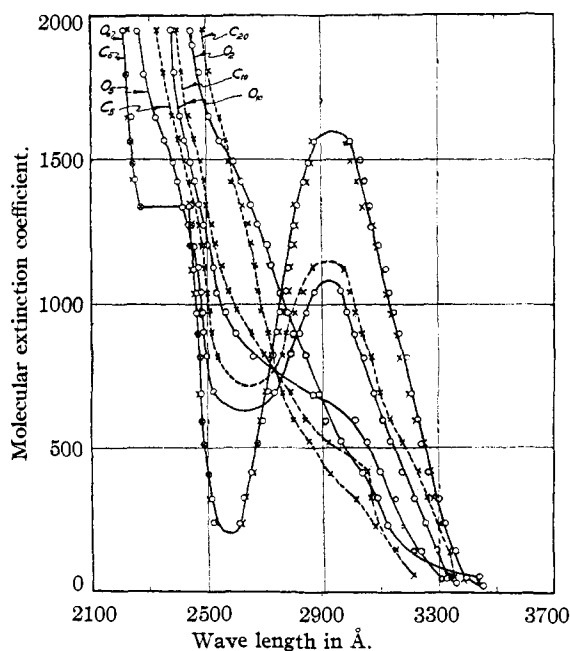


Fig. 1.—Absorption curves of rotenone in ethyl alcohol solutions saturated with O_2 (O) and CO_2 (X) and exposed to sunlight for various periods: O_0 and C_0 , unexposed; O_5 and C_5 , 5 days; O_{10} and C_{10} , 10 days; O_{20} and C_{20} , 20 days. C indicates solutions saturated with carbon dioxide; O indicates solutions saturated with oxygen.

Figure 1 shows the results obtained for the solutions exposed to sunlight for different periods of time. For both of the unexposed solutions, the curves obtained are quite similar. The absorption curves for the two solutions saturated with oxygen and carbon dioxide and kept in the dark for twenty days, together with the curve for the freshly prepared solution, are shown in Fig. 2. The fact that these three curves are identical indicates that oxygen does not play an important role in the decomposition of rotenone in

- (1) Jones, *Ind. Eng. Chem.*, **23**, 387 (1931).
- (2) Jones and Haller, *THIS JOURNAL*, **53**, 2320 (1931).
- (3) Seaber, *J. Soc. Chem. Ind.*, **56**, 168T (1937).
- (4) Cahn, Phipers, and Boam, *J. Chem. Soc.*, 513 (1938).
- (5) Hsieh, Ke, Ts'ai and Wang, *J. Chinese Chem. Soc.*, **6**, 40 (1938).
- (6) Jones, et al., *J. Econ. Entomol.*, **26**, 451 (1933); *C. A.*, **27**, 4015 (1933).

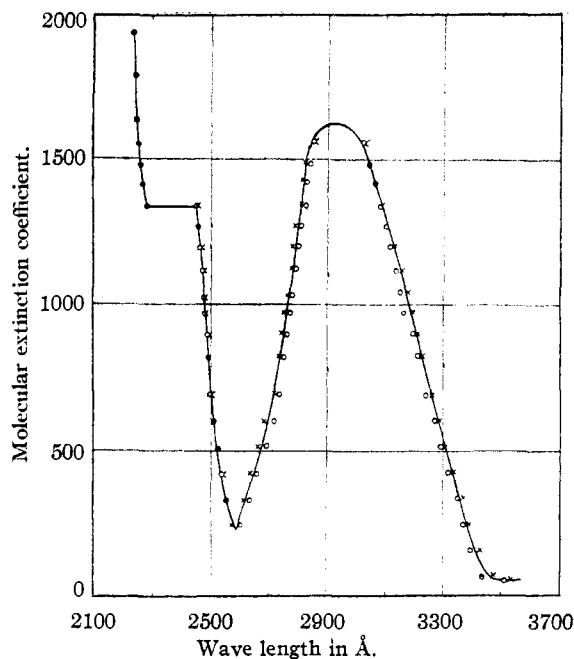


Fig. 2.—Absorption curve of rotenone in ethyl alcohol solution. The plotted curve is for the solution measured immediately after preparation and not saturated with either oxygen or carbon dioxide; the observed values for similar solutions kept in the darkroom for twenty days and saturated with these gases are also indicated: (O) saturated with oxygen, (X) saturated with carbon dioxide.

ethyl alcohol solution. Jones¹ found that, of the various organic solvents studied, rotenone in pyridine solution changed color most rapidly, while in the case of alcohol and benzene solutions the change is almost imperceptible. This suggests

that the oxidation, if occurring, depends to a large extent upon the nature of the solvent used. It would be interesting to study how pyridine differs from alcohol in influencing this decomposition of rotenone, but the fact that pyridine and rotenone both show high absorption in about the same region of the spectrum makes such a study impossible.

On the other hand, the effect of light on the decomposition of rotenone is very marked. It should be noted that the absorption spectra for both of the exposed solutions, that is, the solutions saturated with carbon dioxide and with oxygen (Fig. 1), gradually changed in shape as the period of exposure increased, until the absorption maximum finally disappeared altogether. It is apparent from the curves that for the same period of exposure the absorption spectra of carbon dioxide and oxygen treated solutions differ only slightly. This slight difference could mean only that the effect of oxygen in the photo-decomposition of rotenone is at least very small.

Summary

Study of the absorption spectra of solutions of rotenone in ethyl alcohol, saturated with carbon dioxide and with oxygen, exposed and unexposed to sunlight, showed that oxygen does not decompose rotenone in the dark. In light, however, there is marked decomposition, an effect which does not seem to be due appreciably to the presence of oxygen.

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RECEIVED NOVEMBER 12, 1940

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Raman Spectra of Acetylenes. V. Alkyl Acetylenes

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The main purpose of this series of papers¹ has been to determine what changes occur in the 2200 cm^{-1} region of the Raman spectra of acetylenic compounds when various groups are adjacent to the triple bond carbon and thus to obtain additional information in regard to the occurrence of more lines in this region for disubstituted than for monosubstituted acetylenes. The considerations given in paper IV indicate that some of the additional weak lines are due to isotopic molecules containing a carbon atom of mass thirteen, as

(1) I, *THIS JOURNAL*, **60**, 2664 (1938); II, *ibid.*, **61**, 3546 (1939); III, *ibid.*, **62**, 3185 (1940); IV, *J. Chem. Phys.*, **9**, 390 (1941.)

was suggested for dimethylacetylene by Glockler and Renfrew² and by Crawford.³

An interesting observation⁴ has been made in the case of 6-dodecyne. When this compound was allowed to stand in contact with air, an oxygen atom replaced the two hydrogen atoms on one of the carbon atoms adjacent to the triple bond carbon. The resultant 6-dodecynone-5 had only a single line at 2212 (10), whereas the parent 6-

(2) G. Glockler and M. M. Renfrew, *ibid.*, **6**, 340 (1938); *ibid.*, **6**, 408 (1938).

(3) B. L. Crawford, Jr., *ibid.*, **7**, 555 (1939).

(4) M. J. Murray and Forrest F. Cleveland, *THIS JOURNAL*, **63**, 1363 (1941).