in solution[4] would appear to hold for the sensitized gas phase reaction[6]:

$$\text{(1a)} \quad I_2 + h\nu \longrightarrow I_2^* + M \longrightarrow 2I \qquad \text{Green}$$

$$\text{(1b)} \quad I_2 + h\nu \longrightarrow I + I' \qquad \text{Blue}$$

$$\text{(2)} \quad C_2H_4I_2 + I \longrightarrow C_2H_4I + I_2 \qquad E_{\text{act.}} = 11.8 \text{ kcal.}$$

The light used here causes dissociation of iodine, and the temperature is high enough for reaction 2 to go. The latter reaction probably causes a chain reaction in the gas phase just as in solution[4] and can explain the observed increase in rate.

Photochemical Decomposition.—Absorption of ethylene iodide in solution[3] begins at about 3500 Å. and extends to shorter wave lengths. The absorption spectrum of the gas is not known. With ethylene iodide at a pressure of 6 mm. Hg and a maximum iodine pressure of 0.5 mm. Hg the 3650 and 3341 Å. lines are only very weakly absorbed, but 3130 Å. triplet almost completely absorbed. The corex filter does not remove all of λ 4046, but any decomposition caused by this line is small since the absorption coefficient of iodine is small here.

Rate measurements were made during exposure to light and then for a period after shutting off the arc. From the latter data the thermal rate obtained during photolysis was readily estimated. The combined thermal and light rate in one run was 0.313 mm./min. and the estimated thermal rate 0.102 mm./min., a marked increase due to irradiation.

The mechanism for the photolysis in the gas phase and in solution is probably the same as that given above except that reactions 1a and 1b are replaced by

$$\text{(1c)} \quad C_2H_4I_2 + h\nu \longrightarrow C_2H_4I + I$$

Reaction 1c is possible since the wave lengths used supply more than sufficient energy to break the C–I bond.[3] Reaction 2 is not important in the photolysis in solution at room temperature, but at the temperature used here this reaction probably causes a chain reaction in gaseous ethylene iodide just as in the photo-sensitized decomposition in solution.

It was not deemed feasible to continue the investigation because the thermal decomposition is heterogeneous and also because the thermal rate constitutes such a large part of the photochemical rate. Furthermore, the system is so restricted by the low vapor pressures of ethylene iodide and iodine that their concentrations could not be varied over a sufficiently wide range to determine their effects upon the rate.

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(6) *Cf.*, Ogg, THIS JOURNAL, **58**, 607 (1936).

Studies in Organic Peroxides. VII. Dinicotinyl Peroxide[1]

BY NICHOLAS A. MILAS AND PAUL C. PANAGIOTAKOS[2]

Although acyl peroxides have been known for some time, none of the pyridine or quinoline group are known. In connection with other investigations we have now prepared dinicotinyl peroxide by the interaction of nicotinyl chloride with sodium peroxide. The procedure was as follows:

A solution of 9.6 g. of nicotinyl chloride prepared by the method of Meyer and Graf[3] in 50 cc. of anhydrous ether was added dropwise over a period of one and one-half hours to a well-stirred mixture of 2.8 g. of sodium peroxide and about 28 g. of ice, the temperature being maintained between 0 and −5°. A deep yellow coloration was formed momentarily when the chloride came in contact with the sodium peroxide. The mixture was finally stirred for an additional hour whereby a solid separated which was removed by filtration at 0°, washed thoroughly with ice water and dried at room temperature in a dust-proof chamber. A yield of 2 g. was obtained having a m. p. of 84–87°. A purer product but in smaller yields was obtained when dioxane was used instead of ether to dissolve the nicotinyl chloride. The crude peroxide was recrystallized from a 50-50 mixture of chloroform and purified petroleum ether; m. p. 88–89°, the melt solidified at 140° and remelted at 175°. In the dark the peroxide is stable but decomposes slowly into a yellow solid when exposed to light.

Anal. Calcd. for $C_{12}H_8O_4N_2$: C, 59.1; H, 3.28; active (O), 6.56. Found: C, 59.8, 59.1; H, 4.6, 4.54; active (O), 6.1, 6.46.

Due to the explosiveness of the peroxide, the combustion analyses were not always satisfactory and the high value obtained for hydrogen is not significant.[4]

An attempt to prepare dinicotinyl peroxide hydrochloride from nicotinyl chloride and hydrogen peroxide in anhydrous ether was not successful.

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(1) For contribution VI, THIS JOURNAL, **61**, 2430 (1939).

(2) Present address: Lowell Textile Institute, Lowell, Mass.

(3) Meyer and Graf, *Ber.*, **61**, 2205 (1928).

(4) *Cf.* Stoll and Scherer, *Helv. Chim. Acta*, **13**, 142 (1930); Marvel and Nichols, THIS JOURNAL, **60**, 1455 (1938).

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