a derivative of ergosterol (C_{28}) exists in higher plants is not surprising since it has been shown that ergosterol, itself, is present in numerous phytosterols. Cottonseed sterols have been reported to contain 5% of ergosterol.[5] We have some indication that Δ^5-ergostenol comparable in structure to β-sitosterol and cholesterol also exists in nature, although its isolation in pure form has not yet been accomplished.

(5) Windaus and Bock, *Z. physiol. Chem.*, **250**, 258 (1937).

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Photochemical Investigations. V. The Photolysis and Iodine Sensitized Decomposition of Gaseous Ethylene Iodide

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The thermal decomposition of ethylene iodide has been investigated in the gas phase[1] at 195–230° and in carbon tetrachloride solution[2] at 40–152°. A comparison by extrapolation of the rates in the gas phase and in solution shows that the reaction is apparently the same in both phases. The direct[3] and iodine sensitized[4] photolyses of ethylene iodide have been done in carbon tetrachloride solution but, prior to this work, not in the gas phase.

Experimental

The all-glass reaction system, which was sealed off from the main pumping line during each run, consisted of a 500 cc. flask which could be evacuated to 10^{-3}–10^{-4} mm., a magnetic hammer to break ampules containing a weighed amount of ethylene iodide, and an α-bromonaphthalene manometer connected to the flask through a long spiral of capillary tubing. This tubing and a buffer of ethylene prevented ethylene iodide and iodine from diffusing into the manometer. The reaction system, except the manometer and the exposed tubing (heated electrically), was thermostated at 80°. In order to prevent undue thermal decomposition at the start of a run, the reactants were brought rapidly to 80°. Assuming that ethylene iodide is a perfect gas and extrapolating the vapor pressure data[5] to 80°, 0.042–0.044 g. gave a pressure of about 52 mm. (all pressures on the α-bromonaphthalene scale except where noted), which was less than its saturation pressure. The initial pressures estimated from final pressure readings compared favorably with the calculated values.

The light source for the photo-sensitized decomposition was a 500-watt tungsten lamp. One run was made with the lamp and a Corning filter no. 401, which cut out all light below λ 5000 Å. A mercury arc, used with a Corning red-purple corex filter to remove visible light, was the source of ultraviolet for the direct photolysis.

Thermal Decomposition.—According to Arnold and Kistiakowsky,[1] the decomposition in the gas phase becomes heterogeneous at 195°. The time necessary to decompose thermally any amount of ethylene iodide in carbon tetrachloride solution, providing the combined and free iodine concentrations are known, can be calculated from Polissar's[2] equation. In the gas phase at 80° it was found experimentally that sixty-eight minutes were required to decompose 10% (10 to 20% decomposition), but in solution, at the same temperature and concentration, the time to decompose this same amount was calculated to be 3×10^5 minutes. Since the decomposition is probably homogeneous in solution, the gaseous thermal decomposition at 80° would appear to be heterogeneous. This heterogeneity probably accounts for the lack of agreement found in the thermal rates. At similar total pressures, the rates for the slowest and fastest runs were 0.060 and 0.144 mm./min., respectively. However, a plot of pressure increase *vs.* time gave smooth curves in all runs.

Photo-sensitized Decomposition.—Since the thermal rate of decomposition could not be reproduced, the increase in rate caused by illumination was obtained by allowing the reaction to take place in the dark (to obtain the thermal rate) before turning on the light to obtain the combined light and dark rate. In the run using light of λ = 5000 Å., the rate before illumination was 0.086 mm./min. On exposure, the rate increased to 0.129 mm./min., an increase of 0.043 mm./min. The largest thermal increase for a corresponding period in a dark reaction was 0.022 mm./min. In a similar manner but with the full light of the 500-watt lamp, the increases over the thermal rates were 0.153, 0.157, 0.144 mm./min. for three experiments.

The large increase in rate with the full light of the 500-watt lamp is caused only partially by the blue light made available by removal of the filter. The maximum transmission of the green filter was only about 20% at 5300 Å.; therefore the removal of the filter increased the intensity in this region fivefold, and most of the increase in rate is probably due to this increase in intensity.

The mechanism given for the sensitized reaction

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(1) Arnold and Kistiakowsky, *J. Chem. Phys.*, **1**, 166 (1933).

(2) Polissar, This Journal, **52**, 956 (1930).

(3) De Right and Wiig, *ibid.*, **57**, 2411 (1935).

(4) Schumacher and Wiig, *Z. physik. Chem.*, **11B**, 45 (1930).

(5) Mooney and Ludlam, *Proc. Roy. Soc. Edinburgh*, **49**, 160 (1929).

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

(1a) $I_2 + h\nu \longrightarrow I_2^* + M \longrightarrow 2I$ Green
(1b) $I_2 + h\nu \longrightarrow I + I'$ Blue
(2) $C_2H_4I_2 + I \longrightarrow C_2H_4I + I_2$ $E_{act.} = 11.8$ 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

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

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).

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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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