[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF THE AMERICAN TOBACCO COMPANY]

The Effect of Ultraviolet Radiation on Nicotine

BY C. H. RAYBURN, W. R. HARLAN AND H. R. HANMER

The observation that nicotine and its salts become yellow on exposure to light has led to several studies of its decomposition. Ciamician and Silber[1] exposed nicotine to sunlight from May to November. Methylamine, nicotinic acid and oxynicotine were formed. Custis[2] observed that nicotine solutions exposed to light in absence of oxygen were not decomposed. Pacini and McGuigan[3] and Higgins, Ewing and McGuigan[4] found a loss of toxicity and vasopressor activity in nicotine irradiated with a mercury arc. Wakeham and Tracy[5] and Wakeham and Johnston[6] reported a great decrease of toxicity with short periods of irradiation but further irradiation restored the toxicity. Gant[7] showed that nicotine was destroyed on irradiation and that further irradiation did not restore the toxicity or the vasopressor activity. Both ultraviolet light and oxygen were necessary for decomposition. Methylamine and nicotinic acid were identified. All products which were non-volatile with steam were calculated as nicotinic acid from the results of a Kjeldahl determination. The fact that the sum of the nicotine and nicotinic acid recovered by Gant[7] was more than 100% for short periods of irradiation indicates the presence of a non-volatile intermediate product still containing two nitrogen atoms.

Investigations in this Laboratory showed that non-volatile products were formed which gave insoluble picrates. A picrate was isolated which was found to be identical with the picrate of the oxynicotine prepared from hydrogen peroxide and nicotine by Pinner and Wolffenstein.[8] The melting point of oxynicotine picrate was found to be 169° instead of 154–158° as reported.[8] This melting point agrees with that found for the picrate of an oxynicotine produced by sunlight.[1] The formation of oxynicotine on irradiation of nicotine may be responsible for the initial loss of basicity and toxicity, as Pinner and Wolffenstein report their product to be only weakly basic, and Sabatucci[9] found oxynicotine to be only one-fifth as toxic as nicotine. The recovery of nicotine on treating oxynicotine with reducing agents as reported by Auerbach and Wolffenstein[10] was confirmed. The formation of nicotinic acid and methylamine on irradiation of nicotine was also confirmed.

Experimental

Irradiation Products of Nicotine.—Ninety-nine per cent. nicotine[11] was distilled *in vacuo*. The middle fraction comprising one-third of the total was taken for the experiment.

Five grams of nicotine in 500 cc. of water was placed in a 25 × 15 cm. Pyrex dish with a flat bottom. The solution was irradiated with light from a 220-volt d. c. horizontal type General Electric Uviarc at a distance of 25 cm. The intensity of irradiation in the region 2250–3050 Å. was estimated by the manufacturer to be 2290 microwatts per sq. cm. under these conditions. The temperature of the solution rose to 60–65° during the irradiation. Water lost by evaporation was replaced with distilled water at frequent intervals. After twenty hours the irradiation was discontinued. The solution, which was brown and acid to litmus, was made alkaline with barium hydroxide and distilled with steam, concentrating to a volume of about 75 cc. during the distillation. When a few drops of the distillate no longer gave a precipitate with silicotungstic acid, the distillation was discontinued. Methylamine was identified in the distillate by formation of 2,4-dinitromethylamiline according to the method of Walton.[12] The alkaline residue remaining in the flask was extracted with chloroform. The chloroform was evaporated *in vacuo*, the residue was dissolved in water and excess picric acid was added. A large amount of an oily precipitate formed at once. After standing for several days, clusters of yellow crystals formed in the mother liquor and at several points on the walls of the beaker and on the stirring rod. These were carefully separated from the other material and recrystallized from hot water, m. p. 169°. The alkaline solution remaining from the chloroform extraction was treated with carbon dioxide, filtered, and decolorized with animal charcoal. The solution was evaporated to dryness *in vacuo* and the residue was extracted with alcohol. The alcohol-insoluble salts were dissolved in water and treated with just sufficient sulfuric acid to precipitate the barium. The solution was evaporated *in vacuo* to a sirup. After several days crystals formed which were recrystallized from water, m. p. 232°. A mixture with pure nicotinic acid melted at 232–233°.

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[1] Ciamician and Silber, *Ber.*, **48**, 181 (1915).

[2] Custis, *J. Franklin Inst.*, **184**, 849 (1917).

[3] Pacini and McGuigan, *J. Pharmacol.*, **39**, 241 (1930).

[4] Higgins, Ewing and McGuigan, *ibid.*, **42**, 213 (1931).

[5] Wakeham and Tracy, *ibid.*, **44**, 295 (1932).

[6] Wakeham and Johnston, THIS JOURNAL, **55**, 1601 (1933).

[7] Gant, *J. Pharmacol.*, **49**, 408 (1933).

[8] Pinner and Wolffenstein, *Ber.*, **24**, 61 (1891).

[9] Sabatucci, *Atti accad. Lincei*, **16**, 520 (1932).

[10] Auerbach and Wolffenstein, *Ber.*, **34**, 2411 (1901).

[11] Furnished by Tobacco By-Products and Chemical Corporation.

[12] Walton, *J. Chem. Soc.*, **127**, 40 (1924).

Oxynicotine.—Oxynicotine was prepared from hydrogen peroxide and nicotine according to the method of Pinner and Wolffenstein.[8] The crude oxynicotine was washed with acetone until a pure white product was obtained. The picrate was prepared and recrystallized from hot water, m p. 169°. A mixture with the crystalline picrate obtained from the irradiation products of nicotine also melted at 169°.

A solution of 0.196 g. of oxynicotine was treated with 1 g. of stannous chloride and 5 cc. of concd. hydrochloric acid for one hour at room temperature. Excess barium hydroxide was then added and the solution was distilled with steam. Nicotine was determined in the distillate with silicotungstic acid; recovered 0.154 g. of nicotine (85.1%). The picrate melted at 222°, and a mixture with nicotine dipicrate melted at 222°. The rotation was determined in dilute water solution, $[\alpha]^{25}\text{D}$ −75°.

Summary

1. Oxynicotine, methylamine and nicotinic acid are formed during the ultraviolet irradiation of nicotine.

2. The oxynicotine formed by irradiation is identical with that formed by the hydrogen peroxide oxidation of nicotine.

3. Oxynicotine can be reduced to optically active nicotine.

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Densities and Refractive Indices of Liquid Paraffin Hydrocarbons[1]

BY MAURICE L. HUGGINS

Many studies have been made of relationships between the structures of hydrocarbons and their densities and refractive indices. Nevertheless, in view of the recent publication[2–10] of extensive tables giving these properties for many compounds for which data have not been available until recently, a new attack on the problem would seem to be in order. This paper reports some results of such an attack. It deals only with *densities* (in g./cc. and *refractive indices* (for the sodium D lines) of *paraffin* hydrocarbons in the *liquid* state at 20°C.

Density

Kurtz and Lipkin[11] have recently made a careful and valuable study of the densities and molecular volumes of saturated hydrocarbons, using most of the new data. They deduced the equations

$$V = 32.2 + 16.26n \qquad (1)$$

for normal paraffins, and

$$V = 31.2 + 16.28n \qquad (2)$$

for all paraffins, the constants being averages computed from experimental data for many compounds. Here, n is the number of carbon atoms in the molecule, and V is the molal volume, related by definition to the density ρ and the molecular weight M by the equation

$$V = \frac{M}{\rho} \qquad (3)$$

This paper, insofar as it deals with densities, may be considered an extension and refinement of Kurtz and Lipkin's work, in an attempt to correlate the structural details of the paraffin molecules with their volumes.

Although the experimental data for normal paraffins agree fairly well with a linear equation of the form of Equation 1, as shown in Fig. 1, the values for the short chain compounds show significant deviations. This is evident from an inspection of Fig. 2. To agree with any equation of the form of Equation 1, the points should fall on or near a straight line. Good agreement—within the probable experimental error of most of the individual values—can be obtained by including a term of the form constant/n or, alternatively, constant/V. We tentatively choose the former, merely because it is simpler for our purpose.

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[1] Presented at the Detroit meeting of the American Chemical Society, September, 1940. Some of the material herein was also presented at the Cincinnati meeting, April, 1940.

[2] C. E. Boord, "Science of Petroleum," Vol. II, p. 1349, Oxford Univ. Press, 1938.

[3] D. B. Brooks, F. L. Howard and H. C. Crafton, *J. Research Natl. Bur. Standards*, **23**, 637 (1939).

[4] D. B. Brooks, F. L. Howard and H. C. Crafton, *ibid.*, **24**, 33 (1940).

[5] G. L. Eaton, "Science of Petroleum," Vol. II, p. 1302, Oxford Univ. Press, 1938.

[6] G. Egloff, "Physical Constants of Hydrocarbons," Vol. I, New York, Reinhold Publishing Corporation, 1939.

[7] A. V. Grosse and G. Egloff, "Physical Constants of Paraffin Hydrocarbons," Universal Oil Products Co., Booklet 219, 1938.

[8] A. V. Grosse and Richard C. Wackher, *Ind. Eng. Chem., Anal. Ed.*, **11**, 614 (1939).

[9] A. L. Ward and S. S. Kurtz, Jr., *ibid.*, **10**, 559 (1938).

[10] J. P. Wibaut, H. Hoog, S. L. Langedijk, J. Overhoff and J. Smittenberg, *Rec. trav. chim.*, **58**, No. 4, 329 (1939).

[11] S. S. Kurtz, Jr., and M. R. Lipkin, paper presented at the Boston meeting of the American Chemical Society, September, 1939.