[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY, AND THE LABORATORY OF GENERAL PHYSIOLOGY, HARVARD UNIVERSITY]

Piperidine Metavanadate, a New Light-Sensitive Compound

BY OSKAR BAUDISCH AND F. L. GATES

The organic base piperidine forms with vanadic acid the salt $C_5H_{11}N \cdot HVO_3$, piperidine metavanadate, which has not been previously reported in the literature. It is a white solid, stable when preserved in the dark at room temperature. Exposed to summer sunlight the white powder becomes brown immediately, and black within a few seconds. Diffused daylight produces the same change more slowly. The odor of free piperidine becomes very evident the instant darkening occurs.

If the black product of light-exposure is allowed to stand in the dark in contact with air and dilute piperidine, the light-reaction is reversed and piperidine metavanadate is re-formed. This reversal must be an oxidation process, since it does not occur in the absence of oxygen, and since it is effected rapidly by dilute hydrogen peroxide. Therefore the light-process itself must be a reduction. The reducing action of cysteine hydrochloride on piperidine metavanadate causes the formation of a black product similar to that produced by exposure to light. However, the black product of light-exposure has not been further investigated at this time.

Spectrographic analysis of the light sensitivity of piperidine metavanadate shows that it reacts in the near and middle ultraviolet regions. The longest wave length which visibly affects it is λ 391 mμ. This is just at the boundary between the shortest wave lengths of visible light and the long wave length ultraviolet. Darkening of the metavanadate occurs down to the shortest wave lengths at which sufficient energy could be obtained with the mercury arc to affect silver chloride paper. Dr. Theodore Lyman has very kindly exposed the dry substance in the region between λ 160 mμ and λ 120 mμ, and found that it remained unchanged. Afterward the same sample darkened normally in sunlight.

The spectral absorption coefficients of piperidine metavanadate samples have been obtained. On the basis of a molecular weight of 185.1, they give the curve of Fig. 1. Piperidine metavanadate therefore may be said to show continuous absorption increasing toward shorter wave lengths in the ultraviolet. Dr. Lyman's results presumably indicate a fall in absorption at shorter wave lengths. Piperidine itself shows increasing absorption in the same ultraviolet region as the metavanadate, but its molecular absorption is only about one-thousandth as great.

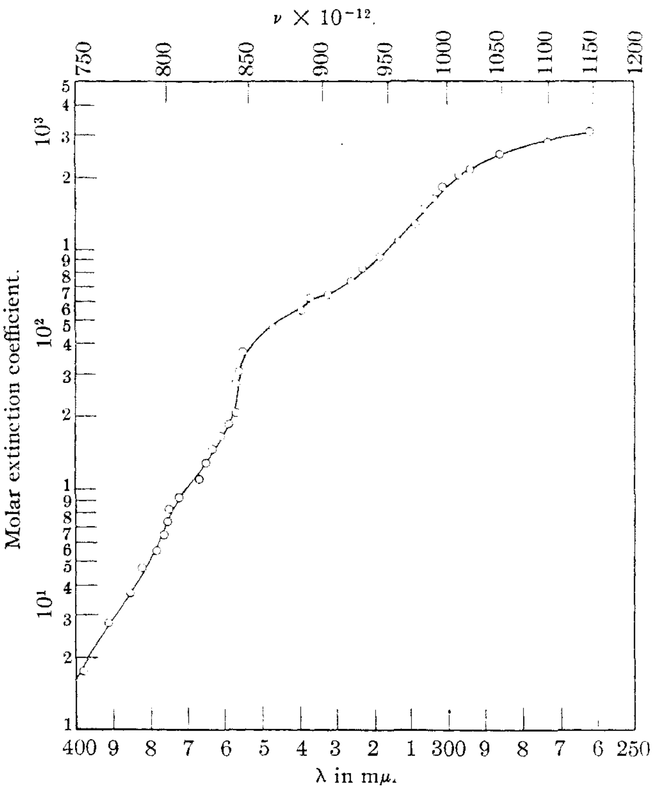

Fig. 1.—Piperidine metavanadate.

Experimental Part

Preparation of Piperidine Metavanadate.—Pure Eastman piperidine (5.0 g.) and 15 g. of water were placed in a small Erlenmeyer flask and heated nearly to boiling. One gram of amorphous vanadium pentoxide (vanadic acid) was added. The mixture was shaken, being kept at the boiling temperature until all the oxide was dissolved. The solution generally contained a small amount of dark green sediment, which was filtered out on a quantitative filter. The filtrate was clear and slightly yellowish. It was placed in a large beaker and in the darkened room (artificial light is relatively safe, but daylight must be excluded) precipitated with six volumes of acetone. The covered vessel was kept in the dark for one or two hours, then the contents filtered. The residue on the filter was washed with acetone and air dried away from light. So prepared, piperidine metavanadate is very pure and does not need further purification. The yield is 2.0 g. or about 98% of the theoretical. Purification can be effected by dissolving in water and precipitating with acetone.

Pure piperidine metavanadate is obtained as a white powder made up of small colorless plates. It is readily soluble in from five to six parts by weight of water at room temperature. It is rather soluble in alcohol, but quite insoluble in acetone, ether, benzene, chloroform and carbon tetrachloride. Piperidine metavanadate as prepared contains no water of crystallization and, protected from light, does not lose piperidine in a vacuum desiccator over sulfuric acid.

Anal. Calcd. for $C_5H_{11}N \cdot HVO_3$; V, 27.54; N, 7.57. Found: V, 27.65, 27.49, 27.51; N, 7.54, 7.40.

Exposure of Samples to Light.—Piperidine metavanadate behaves similarly whether exposed to light uncovered or under glass, Pyrex or quartz. Its water solutions in sunlight become black colloidal solutions. The metavanadate in suspension in piperidine or benzene becomes black in light. Chloroform and carbon tetrachloride in light cause side reactions. Ammonium metavanadate is unaffected by light.

Spectrographic Study of Piperidine Metavanadate.—Piperidine metavanadate was spread evenly on a glass slide and exposed two hours to the ultraviolet radiation of a quartz mercury arc dispersed by a quartz monochromator. The first darkening was visible in two or three seconds at λ 365 mμ.

The spectral absorption measurements were made by the equal density photographic method using micro-Baly tubes, a Judd-Lewis quartz photometer, a Hilger quartz spectrograph, and a tungsten-steel spark. Water solutions of piperidine metavanadate were used.

We are greatly indebted to Rollin D. Hotchkiss for his assistance.

Summary

1. The new compound piperidine metavanadate has been prepared and found sensitive to ultraviolet light but not to the visible spectrum. On exposure to ultraviolet light the white compound becomes brown or black.

2. The light-reaction is a reduction process, reversible by oxidizing agents.

3. The ultraviolet absorption spectrum of piperidine metavanadate has been obtained. The absorption of ultraviolet light by piperidine metavanadate is very much greater than that by piperidine.

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Kinetics of Ethylene Polymerization[1]

BY H. H. STORCH[2]

At pressures not very much greater than one atmosphere, the polymerization of ethylene results in the production of considerable quantities of propylene. In fact, Lenher[3] seems to believe that propylene is a primary product of the reaction. Lenher also reports that small amounts of oxygen accelerate the reaction. A study of Pease's data[4] shows that there is a definite increase in the fraction of ethylene reacting per unit time at constant pressure with increasing total time of reaction. This apparent autocatalysis is much greater in the earlier stages of reaction (as shown by the data given below) than in the experiments of Pease.

In the experiments to be described in this paper, an attempt was made to remove oxygen completely and to study the change in composition of the products with time of contact, using a static system and sufficiently short contact times so that only 0.2–2.0% of the ethylene reacted.

Preliminary experiments amply confirmed Lenher's observation concerning the accelerating effect of oxygen. Using ethylene of the grade prepared for anesthesia, it was found that repeated fractional distillations were insufficient to remove oxygen completely, as judged by subsequent condensation of the ethylene on a large surface of metallic sodium and comparison of its polymerization rate with that of ethylene not treated with sodium. In all later experiments the ethylene, after careful fractionation, was stored in a five-liter flask to the outlet of which was attached a 2.5 × 23 cm. tube filled with glass wool covered with "sputtered" sodium. The

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[3] Lenher, THIS JOURNAL, **53**, 3752 (1931).

[4] Pease, *ibid.*, **53**, 613 (1931).