

2. Consideration of the absorption spectra of these two gases leads to the conclusion that the primary photochemical decomposition in nitrogen peroxide, which consists of nitrogen peroxide and nitrogen tetroxide, is due to the tetroxide constituent.

3. The threshold for complete photochemical equivalence is calculated to be at about 3800 Å.

4. The mechanism,  $N_2O_4 \xrightarrow{h\nu} 2NO + O_2(^1S)$ , is proposed to account for the primary photochemical dissociation, and the continuous absorption spectrum of  $N_2O_4$ . The energy changes involved agree closely with thermal data.

<sup>1</sup> Norrish, *J. Chem. Soc.*, Part 1, 761 (1927).

<sup>2</sup> *Ibid.*, Part 2, 1158 (1929).

<sup>3</sup> Dickinson and Baxter, *J. Am. Chem. Soc.*, **50**, 774 (1928).

<sup>4</sup> Harris, *Proc. Nat. Acad. Sci.*, **14**, 690 (1928).

<sup>5</sup> Franck, *Trans. Farad. Soc.*, **21**, 536 (1926).

<sup>6</sup> Franck, Kuhn and Rollefson, *Zeit. Phys.*, **43**, 155 (1927).

<sup>7</sup> Franck and Kuhn, *Zeit. Phys.*, **43**, 164 (1927).

<sup>8</sup> Iredale and Wallace, *Phil. Mag.*, **8**, 1093 (1929).

<sup>9</sup> Urey, Dawsey and Rice, *J. Am. Chem. Soc.*, **51**, 3190 (1929).

<sup>10</sup> Mulliken, *Phys. Rev.*, **32**, 880 (1928).

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## THE STUDY OF ABSORPTION SPECTRA OF ORGANIC COMPOUNDS AT LIQUID AIR TEMPERATURES

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It is well known that certain broad bands in the ultra-violet absorption spectrum of benzene are broken into finer lines at liquid air temperatures. At the suggestion of Professor Linus Pauling we have examined the visible absorption spectra at low temperatures of solutions of porphyrins and certain other colored organic compounds to see if the same phenomenon could be noted. As Professor Pauling has suggested, the characteristic spectrum of a porphyrin, which consists of a number of relatively very narrow bands, is probably due to the fact that the chromophoric groups are protected from thermal disturbances by the large cyclic system; the porphyrins might thus be considered analogous to the rare earths. It might be expected, therefore, that the visible spectrum of a porphyrin would be resolved into narrower bands at low temperatures. The sub-

stances we have studied are protoporphyrin dimethyl ester, phylloporphyrin, chlorin e, bilirubin and pinacyanole. All these substances have strong absorption bands in the visible. Chlorin e and bilirubin like the porphyrins contain pyrrol rings; the relation of the former to the porphyrin is still unsettled, the latter almost certainly does not contain the characteristic porphyrin ring. The photosensitizing dye pinacyanole was chosen because of its relatively narrow band.

Dilute solutions of the materials in alcohol and ether were examined both visually and photographically with a smaller Hilger constant deviation spectrometer. In order to keep the substance at the temperature of liquid air, the solution was placed in a thin walled test tube and congealed by immersion in liquid air in an unsilvered Dewar flask. The test tube was then raised so that about 1 cm. of the gel projected above the surface of the liquid air and the beam of light was passed through this exposed layer. With care, crystallization of the solvent usually could be avoided.

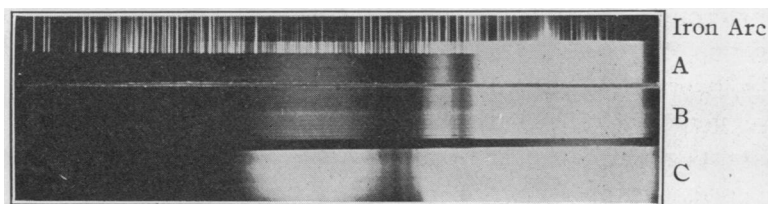


FIGURE 1

Absorption spectrum of a porphyrin at room temperature and in liquid air. (A = room temperature, B and C at liquid air temperature, C longer exposure than B. 10 mg. of protoporphyrin dimethyl ester in 1 liter of ether.)

As judged by visual observation, the widest bands in the porphyrins were broken into fairly uniformly spaced narrow bands. The other substances failed to show this phenomenon. Photographs of the porphyrin spectra at room temperature and at liquid air temperatures brought out the effect even more clearly. (Fig. 1.)

The positions of the narrow bands obtained at low temperatures with protoporphyrin dimethyl ester, were measured by comparison with an iron arc. The narrower band with a center near  $\lambda$  53,630, broke up into three components of frequency 18,462, 18,648, 18,909  $\text{cms.}^{-1}$ . The wider band (center at approx.  $\lambda$  5000) yielded six components: 19,488, 19,668, 19,887, 20,107, 20,328, 20,544  $\text{cms.}^{-1}$ . It is interesting that the frequency differences in the first group are 186 and 260  $\text{cms.}^{-1}$  and in the second 180, 219, 220, 221, 226  $\text{cms.}^{-1}$ . This suggests that the components in each group represent vibrational bands having a common value for the *change* in the vibrational quantum number.

It seems probable that the phenomenon of resolution of bands at low temperatures may be characteristic of compounds having certain cyclic systems. If this is the case a spectroscopic study of solutions of compounds at liquid air temperatures may serve as a ready means of recognizing the presence of such characteristic cyclic systems as are present in the porphyrins. In particular we hope that a differentiation between the porphyrins and the closely related chlorophyll derivatives may be possible. A very large number of these compounds have been prepared in this laboratory in a high state of purity and their spectra at low temperatures will be examined in the near future.

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A CORRECTION

Due to a mistake in the preparation of Table VII, p. 134, in our article on "The Decomposition of Nitrogen Pentoxide at Low Pressures" in these PROCEEDINGS, 16, 129-135 (1930), the time which is given in the first column is incorrect. The values given should each be multiplied by 2.3, the conversion factor for changing from the natural to Brigg's logarithms. The constants given in the Table are correct, because they were calculated with the correct time.

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