

the removal of the copper, as well as the negative results obtained in the hydriodic acid reduction prove that the prosthetic group is neither a porphyrin nor a closely related substance such as a bile pigment.

The stability of the black copper complex and its tendency to form soluble, highly colored complexes with amines (and also denatured albumen) indicates that the compound we have in hand is involved in the union of the copper to the protein in hemocyanin. The function of the prosthetic group thus appears to be the same as that of protoporphyrin in hemoglobin, namely, to provide a basis for a very stable metallic complex. Beyond this analogy, however, there seems to be little or no chemical relationship between the prosthetic groups in limulus hemocyanin and hemoglobin. It should be noted that since limulus hemocyanin differs markedly in its copper content from the hemocyanin of other species,<sup>2</sup> the conclusions we have drawn do not necessarily apply to the nature of the prosthetic group in the other hemocyanins.

We are greatly indebted to Mr. I. S. Danielson for his assistance in procuring the initial material and for carrying through a number of the experiments.

<sup>1</sup> E. Philippi, *Zeit. Physiol. Chemie*, **104**, 88 (1919).

<sup>2</sup> Redfield, Coolidge and Shatts, *J. Biol. Chem.* **76**, 185 (1928).

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## THE PHOTOCHEMICAL DISSOCIATION OF NITROGEN PEROXIDE

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When the substance, nitrogen peroxide, consisting of a mixture of two gases, nitrogen peroxide,  $\text{NO}_2$ , and nitrogen tetroxide,  $\text{N}_2\text{O}_4$ , is illuminated with approximately monochromatic light from a quartz mercury arc, an increase in pressure occurs which is greater than that to be expected from the heating effect of the radiation on the gas. The abnormal rise in pressure has been attributed to photochemical decomposition. Norrish<sup>1</sup> almost exclusively studied the equilibrium involved, and in later work<sup>2</sup> investigated the quantum yield so far as to determine the number of oxygen molecules formed in the reaction system per quantum of light absorbed. One molecule of oxygen was produced for every quantum absorbed in the spectral regions 2700–3160 Å and 3660 Å, while at longer wavelengths of 4050 Å and 4360 Å, 0.37 and 0.0 molecules of oxygen, respec-

tively, were produced for each quantum absorbed. Dickinson and Baxter<sup>3</sup> effectively showed the products of the photochemical decomposition to be nitric oxide and oxygen. The variation of the quantum yield with wave lengths of light used in illumination leads to the belief in a photochemical threshold which must exist between 4050 Å, the region in which dissociation began to take place, and 3660 Å, the region where full photochemical equivalent was observed. The quantum yield at intermediate wave lengths has not been investigated.

Since nitrogen peroxide contains two kinds of molecules, the analysis and formulation of the reaction becomes increasingly difficult. For instance, it was equally as possible to begin upon the assumption that the photoactive species was either the  $\text{NO}_2$  molecule or the  $\text{N}_2\text{O}_4$  molecule. On the other hand, it was not inconceivable that both molecules may be involved. The question can at least be partially solved by a study and

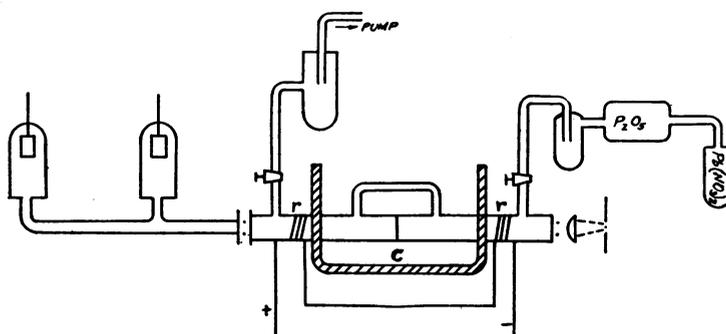


FIGURE 1

review of the existing absorption spectrum data concerning these two gases.

Harris<sup>4</sup> reported the absorption spectrum of nitrogen peroxide to consist of two separate and distinct types of absorption. The first, which was attributed to  $\text{NO}_2$ , extends from the visible region of the spectrum into the ultra-violet as far as 2250 Å, and exhibits a complex banded structure. The second, which is attributed to  $\text{N}_2\text{O}_4$ , begins within the limit of experimental error, at about 4000 Å, and exhibits a *continuous* absorption spectrum which increases in intensity to a maximum at about 3500 Å. These results were confirmed in hitherto unpublished work of the writer. While photographing the absorption spectrum of nitrogen pentoxide, the writer found it necessary to photograph both the absorption spectrum of nitrogen peroxide and nitrogen tetraoxide, since the latter two gases were ultimately produced in the decomposition of the pentoxide, and the presence of either in appreciable amounts would have masked the true absorption spectrum of the pentoxide. Photographs of  $\text{NO}_2$  at the temperature of 140° C. and solid  $\text{N}_2\text{O}_4$  at the temperature of liquid air were taken, the following precautions being observed:

Pure nitrogen peroxide was made from heated lead nitrate, passed over phosphorus pentoxide, and condensed into a trap surrounded by carbon dioxide-ether mush. The trap, the 30-cm. length quartz absorption cell, the drying tube and the lead nitrate bulb were pumped free of air, and the inlet and outlet stopcocks to the absorption cell were closed. By taking the freezing mixture away from the trap, and manipulating the inlet stopcock, any desired quantity of the brown gas could be admitted to the absorption cell. The absorption cell was constructed with two compartments such that light traversing the cell had to pass through three quartz windows. The gas was free to flow from one compartment to the other by way of the by-pass around the inner window. Figure 1 illustrates the apparatus used. The source of continuous ultra-violet light was afforded by a hydrogen discharge tube. The light rays from the discharge tube, after passing the length of the absorption cells, were focused on the slit of the spectrograph. A Hilger E-37 quartz spectrograph was used in addition to a larger E-3 instrument.

A number of successive exposures were taken with  $\text{NO}_2$  gas in the absorption cell, at varying pressures less than atmospheric. The temperature was kept at  $140^\circ$  by means of electrical heating elements which were wrapped the whole length of the absorption cell, and this temperature was measured by means of a thermometer enclosed within the asbestos casing about the cell. These exposures are shown upon plate 1. The complex banded absorption attributed to  $\text{NO}_2$  by Harris begins in the visible region of the spectrum, rises to a maximum at approximately  $3900 \text{ \AA}$ , and then decreases to a minimum intensity at approximately  $3200 \text{ \AA}$ . Apparently,  $\text{NO}_2$  absorbs radiation very weakly in the region  $3200$  to  $2495 \text{ \AA}$ . A second series of bands begin at  $2490 \text{ \AA}$ , the wave lengths of which have been previously determined by Harris, for the reason that they possess a very much simplified appearance in comparison to those bands due to  $\text{NO}_2$  in the visible spectrum.

Plate 1 also shows a photograph made with solid  $\text{N}_2\text{O}_4$ . The following method was used to obtain this photograph. Referring again to figure 1 the gaseous contents of the absorption cell, after photographing the mixture of the two oxides at room temperature, were condensed out upon the inner window, by pouring liquid air into the plaster-of-paris container *C*, which was moulded about the absorption cell. The brown gas, which turned into white crystalline  $\text{N}_2\text{O}_4$  upon the inside window, therefore, formed a semi-transparent layer on both sides of the quartz disk. This was ascertained by viewing the absorption cell, end on, with the eye while the hydrogen discharge tube was turned on. The ends of the absorption cell which protruded from the cold container *C* were kept free from condensed moisture, by means of the electrical heating elements, *r*. This photograph, therefore, shows the region of the spectrum absorbed by

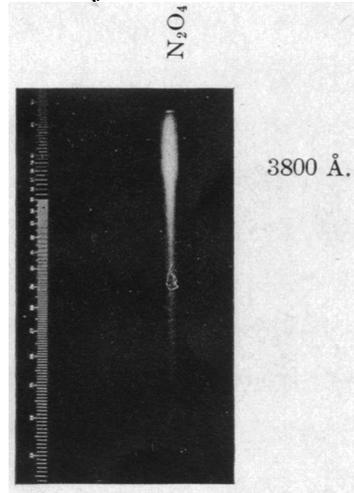
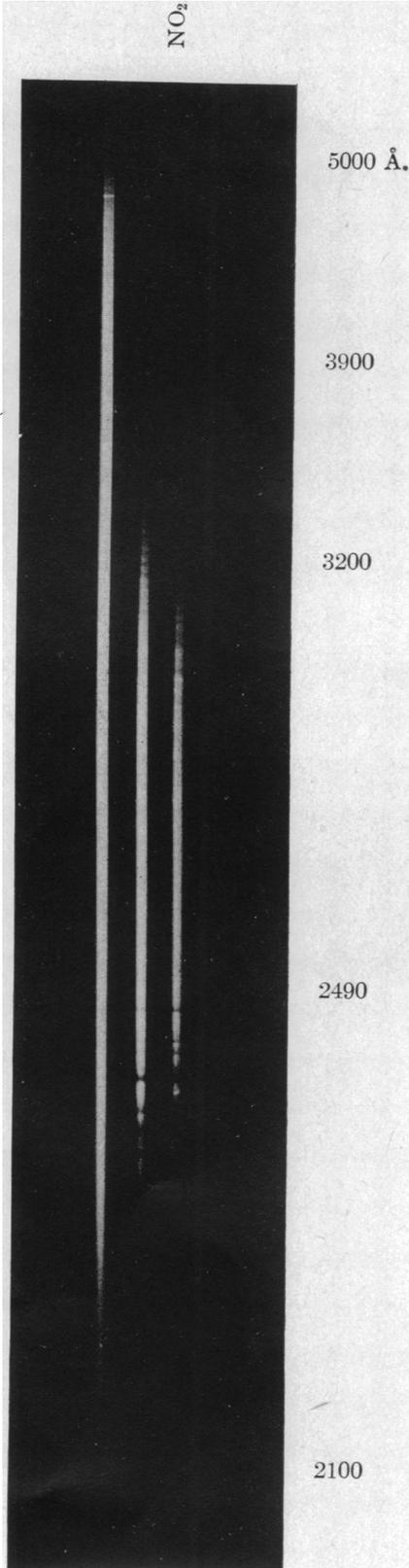


PLATE I.

crystalline  $N_2O_4$  at the temperature of liquid air,  $-182^\circ C$ . Absorption begins, within the limit of experimental error, at about  $3820 \text{ \AA}$ , increasing in intensity toward the shorter wave lengths. Some diffuse light was transmitted below  $3820 \text{ \AA}$ , but this was to be expected, and may be accounted for in reflection of light from crystal face to crystal face in the thin layer. This photograph is doubtless of no other value except that it enables the long wave length limit of absorption to be determined for  $N_2O_4$  while in the crystalline state.

In general, within the limit of experimental error, the light energy of activation should not vary to a great extent, regardless of the state, solid, liquid, or gas, which the molecules might be in. This is not, however, exactly correct. The heat of activation in the gaseous state, according to conventional thermochemical calculations, differs from the heat of activation in the solid state, by an amount of the order of the difference in thermal energy possessed by the substance at two temperatures. The difference in thermal energy in this case may be divided in five separate parts,  $\Delta E_1 = \int_{T_1}^{T_2} C_p dT$ , the energy necessary to raise a mol of  $N_2O_4$  from the temperature of liquid air to its melting point,  $-10^\circ C$ ., plus the heat of fusion,  $\Delta E_2$ , plus  $\Delta E_3 = \int_{T_2}^{T_3} C_p dT$ , the energy necessary to raise the substance from its melting point to its boiling at  $18^\circ C$ ., plus the heat of vaporization,  $\Delta E_4$ , plus  $\Delta E_5 = \int_{T_3}^{T_4} C_p dT$ , the energy necessary to raise the gas from its boiling point to room temperature. The specific heat of nitrogen tetroxide is not known, and for that reason, assumed values must be used. Making use of Kopp's Law,  $C_p$  for solid  $N_2O_4$  is about 22 calories per mol. The first quantity above then becomes  $\Delta E_1 = 3.984$  kilo-calories.  $\Delta E_2$  is 0.034 kilo-calories (I. C. T. value).  $\Delta E_3$  becomes 0.670 kilo-calories, assuming the rough value of 24 calories per mol for the heat capacity of liquid  $N_2O_4$ .  $\Delta E_4$  is probably very small. The specific heat of gaseous  $N_2O_4$  is doubtlessly less than for two mols of  $NO_2$  and is not greater than about 18 calories per mol.  $\Delta E_5$  then becomes 0.126 kilo-calories, and the total change in thermal energy between the temperature of liquid air and the room temperature of  $25^\circ C$ ., is of the order of 4-5 kilo-calories. The long wave length limit observed for  $N_2O_4$  at liquid air temperature is  $3820 \text{ \AA}$  corresponding to 74.6 kilo-calories for the least heat of optical activation to which the molecule is susceptible. Subtracting this value of about 4.5 kilo-calories energy, which must be present in the gas at  $25^\circ C$ . from the heat of activation at  $-182^\circ C$ ., 70.2 kilo-calories is obtained which must correspond to the least energy of optical activation at the higher temperature. This latter