Fig. 1.—Ultraviolet absorption spectra in liquid sulfur dioxide at 1°: curve 1, anthracene; curve 2, s-trinitrobenzene (1 + log molar absorbancy index); points O, anthracene–TNB complex.

further toward longer wave lengths. A specific interaction between anthracene and sulfur dioxide is indicated. This is in agreement with the known formation of complexes between benzene (and certain of its derivatives) and sulfur dioxide.[3]

It must be concluded that the conductivity data provide no evidence in support of the TNB–anthracene complex possessing an ionic nature. Furthermore, the spectrophotometric data provide no evidence for the existence of this complex in liquid sulfur dioxide solution. The spectral evidence for interaction of anthracene and sulfur dioxide suggests that molecules of the latter may effectively displace TNB from its complex with the hydrocarbon. The wide melting range of "complex" recovered from solution in sulfur dioxide supports this suggestion.

It must not be concluded, however, that no new information relevant to Weiss' theory[3] has been obtained. The data for anthracene and TNB lead to significant deductions. Anthracene is shown spectrophotometrically to interact strongly with sulfur dioxide, yet its conductance is no greater than that of TNB which shows no such interaction. The profound change in the anthracene spectrum suggests that all of the anthracene is involved in the interaction. This cannot be proven with the data at hand but a minimum value for the fraction of anthracene interacting can be determined. In inert media the molar absorbancy of anthracene at the sharp 375 mμ peak is at least 8000.[10] In sulfur

(9) L. J. Andrews and R. M. Keefer, THIS JOURNAL, 73, 4169 (1951).

(10) (a) American Petroleum Institute Research Project 44 at the National Bureau of Standards. Catalog of Ultraviolet Spectrograms Serial No. 170, contributed by the Shell Development Co., Emeryville, Calif. (in isoöctane); (b) ref. 5, p. 264 (in carbon tetrachloride); (c) W. V. Mayneord and E. F. M. Roe, Proc. Roy. Soc. (London), A152, 299 (1935) (in ethanol); (d) K. Lauer and M. Horio, Ber., 69, 130 (1936) (in hexane).

dioxide at this wave length it is 5100. If one makes the extreme assumption that anthracene which is interacting with the solvent is completely transparent at this wave length, then it must be concluded that no more than 64% of the anthracene is free. Thus no less than 36% of the hydrocarbon is involved in the interaction. In view of the agreement of the spectral data for this compound with Beer's law, this holds at all concentrations. From these considerations it must be concluded that, contrary to the suggestion of Weiss,[11] the interaction between anthracene and sulfur dioxide cannot consist of complete electron transfer to yield the (radical) ion pair $(C_{14}H_{10})^+$ $(SO_2^-)$. Such an ion pair would dissociate to about the same extent[12] as the pair triphenylcarbonium chloride which has been shown[7,12] to have a dissociation constant in sulfur dioxide no smaller than $10^{-3}$ at 0°. It would yield enormously greater conductances than those observed. To the extent that the anthracene–TNB and anthracene–sulfur dioxide interactions are similar,[2d] doubt is cast on Weiss' picture of the former as well.

(11) Reference 3, p. 250.

(12) N. N. Lichtin and P. D. Bartlett, THIS JOURNAL, 73, 5530 (1951).

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## Observations Concerning Polymorphic Crystalline Modifications of the Phthalocyanines[1]

BY FRANCIS W. KARASEK AND J. C. DECIUS

Phthalocyanine and some of its metallic derivatives exist in two known polymorphic crystalline forms. The α-form is normally produced by dissolving the compound in concentrated sulfuric acid and precipitating it by dilution with ice-water. A micro crystal is formed whose structure is not known. The β-form may be produced by low pressure sublimation according to the technique of Barrett.[2] This procedure produces a well-defined monoclinic crystal whose complete structure has been determined by Robertson.[3]

In the course of obtaining the infrared absorption spectra of these compounds, it was found necessary to produce a sample with a very small particle size to avoid severe scattering losses at the shorter wave lengths. This was accomplished by subliming a film of the phthalocyanine directly onto a highly polished and relatively cool (below 200°) rock salt plate under a pressure of $10^{-5}$ mm. A

(1) Supported by a Frederick Cottrell Grant from the Research Corporation.

(2) P. A. Barrett, et al., J. Chem. Soc., 1719 (1936).
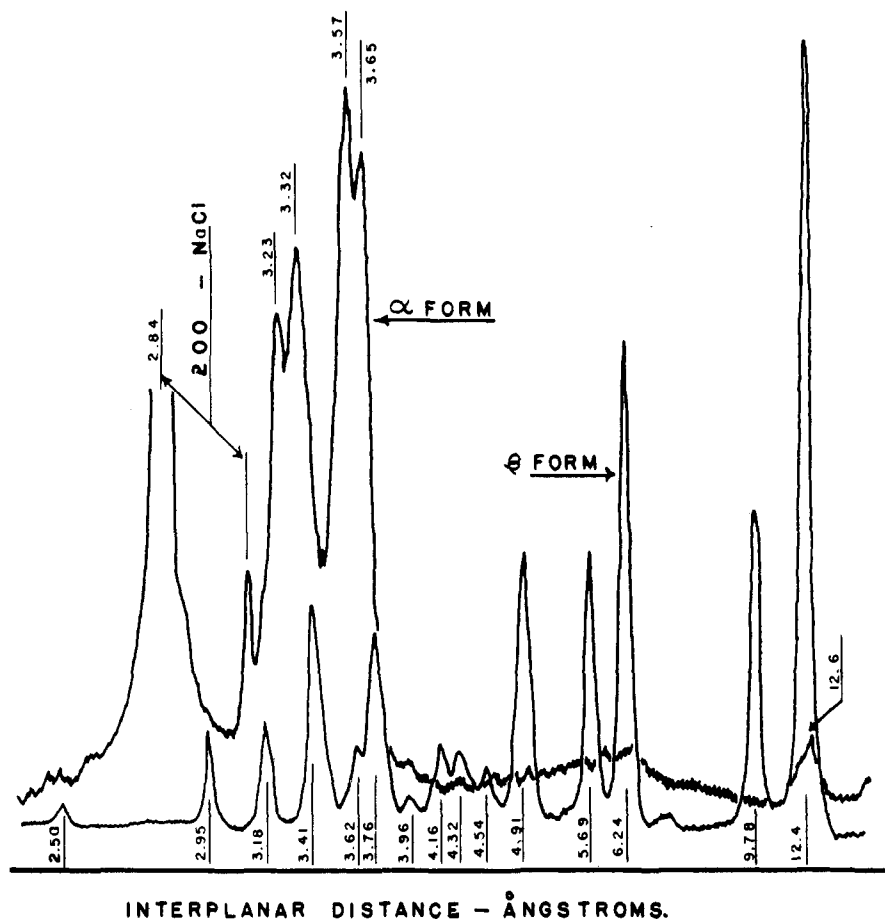
(3) J. M. Robertson, ibid., 615 (1935).

Fig. 1.—X-Ray diffraction patterns of metal-free phthalocyanine.

study of the infrared spectrum[4] and X-ray diffraction pattern of this material revealed that this technique produces the α-form of a phthalocyanine. The average particle size appears to be of the order of a few microns as evidenced by low scattering losses at wave lengths of 3 microns and above. Figure 1 illustrates the X-ray diffraction pattern of the β-form of metal-free phthalocyanine obtained as a powder, and superimposed on the same scale is that of the α-form deposited on a rock salt plate. The decrease in the relative intensity of the diffraction line at 12.6 Å. as compared with the results of Ebert and Gottlieb[5] may be attributed to partial orientation of the crystals produced by sublimation. The β-pattern agrees quite well with that calculated from the data of Robertson.

A preliminary investigation of the pressure dependence of the phase change indicated that the alpha form of metal-free phthalocyanine is produced at sublimation pressures up to 50 mm. The α-form of copper phthalocyanine is produced at pressures up to 0.1 mm.; above this pressure sublimation produces the β-form.

German scientists discovered that an α-β-phase transition occurs for the metal-free and copper phthalocyanine at temperatures above 200°.[6]

(4) D. N. Kendall, 119th A.C.S. Meeting, April, 1951, Abstracts Division of Phys. and Inorg. Chem., 2p.
(5) A. A. Ebert, Jr., and H. B. Gottlieb, This Journal, 74, 2806 (1952).
(6) Fiat, Final Report 1313 Vol. III, U. S. Dept. of Commerce, Washington, D. C., 1948, pp. 345-439.

Barrett's condensation temperature was 400°, which explains why the α-form of metal-free phthalocyanine was never produced by his procedure.

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## The Dissociation of Certain Benzohydryl Ethers

By Ti Li Loo

The report by Kaye[1] and by Harms and Nauta[2] of the dissociation of certain benzohydryl ethers to afford s-tetraphenylethane finds support from work performed by the present author in 1947 in connection with other studies, first during preparation of the oxide of benzohydrylallylether, and again during the reaction of 1-benzohydryl ether of 3-chloro-1,2-propanediol with piperidine.

In the first instance, an unsuccessful attempt was made to prepare by the procedures of Brunel[3] and Bougault[4] the oxide (III) from benzohydryl allyl ether (I), through the iodohydrin (II) (not isolated). Upon distilling in vacuo an ethereal solution containing the supposed iodohydrin (II), a small amount of s-tetraphenylethane (IV) was obtained.

(1) I. A. Kaye, This Journal, 73, 5468 (1951); I. A. Kaye, I. C. Kogon and C. Parris, ibid., 74, 403 (1952).
(2) A. F. Harms and W. T. Nauta, Rec. trav. chim., 71, 431 (1952).
(3) L. Brunel, Compt. rend., 135, 1055 (1902).
(4) J. Bougault, Bull. soc. chim., 25, 444 (1901).