peak. All three gave identical decay curves, corresponding to the disintegration rate of Nb^{95}. When this experiment was repeated a somewhat different curve was obtained. Again three peaks were found, but these were rounded, and the areas under the first and third were approximately equal and greater than that of the second. Brown and Rieman[1] also report that their elution bands were not exactly reproducible.

This departure from the expected type of elution band can probably be attributed to the slow establishment of equilibrium among various ionic species which are present. These ions would not necessarily have to have different charges, as in the case of the thiocyanate complexes of chromium,[3] but may contain different numbers of chloro-, oxy- and hydroxy-groups. Elution with 6.0 M hydrochloric acid gives the usual symmetrical curve.

This work was done under the auspices of the Atomic Energy Commission.

[3] E. L. King and E. B. Dismukes, *ibid.*, **74**, 1674 (1952).

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The State of Anthracene, *sym*-Trinitrobenzene and their 1 : 1 Complex in Liquid Sulfur Dioxide Solution

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Numerous investigations of molecular complexes between polynitroaromatic compounds and unsaturated hydrocarbons and their derivatives, both in the crystalline state and in solution, have led to varying interpretations as to the nature of the binding forces involved.[2] The investigation reported here was directed toward testing the proposal of Weiss[3] that such complexes are produced by complete transfer of an electron and are ionic in nature. The conductivity behavior and ultraviolet spectra of liquid sulfur dioxide solutions of *sym*-trinitrobenzene (TNB), anthracene and their 1:1 complex were accordingly investigated over a range of concentrations.

Experimental

Materials.—Reilly Tar and Chemical Corp. "Scintillation Grade" anthracene was employed, m.p. 215.4–215.5°,[4] strongly fluorescent. It was purified by sublimation at 120° and 1 mm. pressure to yield material melting sharply at 215.4°.[4] Eastman Kodak Co. "White Label" TNB, m.p. 122.2–122.4°,[4] was purified by sublimation at 100° and about 0.001 mm. pressure to yield slightly yellow material melting at 123.2–123.3°.[4] The complex was prepared from the vacuum sublimed components by the method of Briegleb and Schachowskoy.[5] The product consisted of long orange needles, m.p. 163.8–164.0°.[4] The purity of the sulfur dioxide employed in the conductivity measurements[6] and spectrophotometric work[7] is described elsewhere.

Measurements.—Conductivity measurements were carried out at 0.11 ± 0.03° using apparatus and procedures which are described elsewhere.[6] With anthracene and the complex the samples were pumped in the conductivity cell at about 0.001 mm. pressure and 0° for periods of at least 12 hours before sulfur dioxide was admitted. TNB was similarly pumped in only one run but this run did not differ significantly from others with this compound.

After some of the conductivity runs, the solute was recovered by pouring the solution into an evaporating dish and allowing the solvent to evaporate in air. Recovered anthracene melted at 215.2–216.8°.[4] Recovered TNB melted at 123°.[4] Recovered "complex" melted over the range 140–170°[4] even though it looked unchanged.

Spectrophotometric measurements were carried out at 1–2° using apparatus and procedures which are described elsewhere.[7]

Evaluation of Conductivity Measurements.—Solutions of the purified materials possess such low conductivities that, even though the specific conductivity of the solvent usually fell in the range 2.9×10^{-8} to 7.3×10^{-8}, this was normally more than 10% of the total specific conductivity of the most concentrated solutions (about 0.01 molar) and from 22 to 50% of the conductivity of the most dilute solutions (about 0.00005 molar). In this connection it must be emphasized that the measured conductivity of the solvent is highly sensitive to traces of electrolytes desorbed from the electrodes or the walls of the cell. This can be demonstrated by repeated redistillation of the solvent within the cell in the absence of added solute. Thus, in one case, six distillations reduced the solvent conductivity to one-fifth of its initial value. Correction of solution conductivities for solvent conductivity is therefore an approximate procedure. In the present case solute conductivities can be considered known to within a factor of two.

Data and Discussion

The molar conductances (Λ) of anthracene, TNB, and the complex were determined in the concentration range $4 \times 10^{-4}\ M$ to $4 \times 10^{-3}\ M$. The Λ values ("corrected" for solvent conductivity) all fall in the range from 0.02 to 0.7 mho cm.^{2}/mole. The molar conductance of anthracene is somewhat lower than that of TNB at all concentrations. Within the reliability of the data, the conductance of the complex is equal to the sum of the conductances of its components.[8]

The spectral data are summarized in Fig. 1 where molar absorbancy index ($(1/bc) \log (I_0/I)$, b in cm., c in moles per liter) is plotted logarithmically *vs.* wave length. It is apparent that the spectrum of the complex is within experimental error identical with the sum of the spectra of its components.

Solutions of the complex were found to obey Beer's law at 430 mμ (in the concentration range 4.85×10^{-4} to $5.16 \times 10^{-5}\ M$) with a molar absorbancy index of 1350. At this wave length, anthracene solutions were also found to obey Beer's law (in the concentration range 1.16×10^{-3} to $5.06 \times 10^{-5}\ M$) with a molar absorbancy index of 1450. The agreement of these two values is within experimental error.

It is notable that, although the spectrum of TNB in sulfur dioxide solution closely resembles that in carbon tetrachloride,[5] the spectrum of anthracene in sulfur dioxide lacks the fine structure observed in the latter solvent,[5] and extends much

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[1] Taken in part from the A.M. Thesis submitted by June D. White to the Graduate School of Boston University.

[2] (a) G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 67–69; (b) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, pp. 184–185; (c) G. Briegleb, "Zwischenmolekulare Kräfte," G. Braun, Karlsruhe, 1949, pp. 12–15; (d) R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952).

[3] J. Weiss, *J. Chem. Soc.*, 245 (1942).

[4] Capillary melting point, measured with Anschütz-type total immersion thermometer.

[5] G. Briegleb and T. Schachowskoy, *Z. physik. Chem.*, **19B**, 255 (1932).

[6] N. N. Lichtin and H. Glazer, THIS JOURNAL, **73**, 5537 (1951).

[7] P. D. Bartlett and R. E. Weston, Jr., *ibid.*, **74**, in press.

[8] The possibility that the observed conductivities are due to traces of electrolytic impurities cannot be ruled out. Presumably the impurities in the components would be carried into the complex.

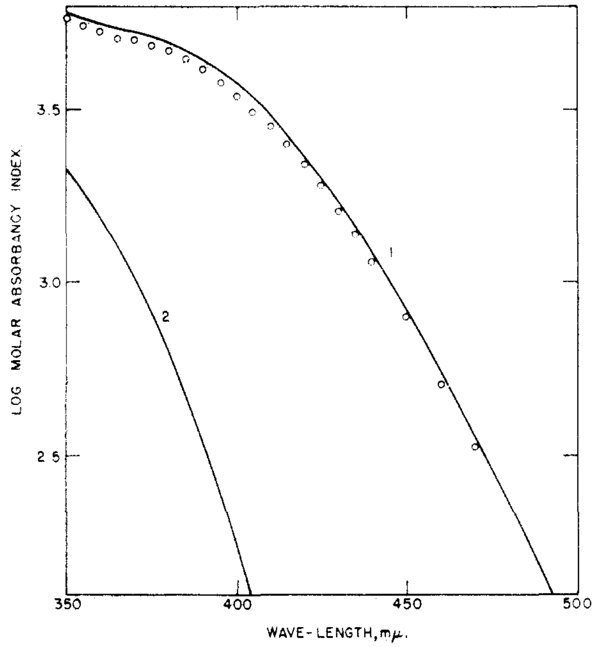

Fig. 1.—Ultraviolet absorption spectra in liquid sulfur dioxide at 1°: curve 1, anthracene; curve 2, s trinitrobenzene (1 + log molar absorbancy index); points O, anthracene–TNB complex.

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.[9]

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 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.

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(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).

(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]

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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

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(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).