found to be present to the extent of about 10 to 20% of the amount of A formed.

The properties of 3,5-dichlorophenetole and 3,5-diethoxychlorobenzene, the expected products of the reaction, have not been previously given. For identification compounds A and B were cleaved with solid, anhydrous $AlCl_3$ to give the corresponding phenols. The benzoate of the phenol from compound A and the hydrate of the phenol from compound B were prepared. Table I summarizes the properties of compound A, compound B, 3,5-dichlorophenetole, 3,5-diethoxychlorobenzene and their indicated derivatives.

Since the carbon analyses for compound B are high it would appear that other products also were formed in small amounts; these were not identified. It seems clear that the compounds given are the major ones and the properties of 3,5-dichlorophenetole are fairly well defined.

Kinetic Results.—The kinetic studies data of the reaction are given in Table II where T is the temperature of the reaction in degrees centigrade, d is the density of alcohol at the temperature T, t is the time in minutes, ml. H^+ is the volume in milliliters of standard (0.02503 N) acid used in the titration, k is the calculated second-order rate constant in liter mole min.

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Absorption Spectra and Basicity of 2,3-Diaminodibenzofuran[1]

BY EUGENE SAWICKI AND F. E. RAY

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In connection with an extensive investigation in this Laboratory on the chemical and physical properties of the aromatic carcinogens, it was of interest to determine the basicity of 2,3-diaminodibenzofuran as compared to 3-aminodibenzofuran. In the latter compound the amino group is in the extended para position as it is in all the known biphenylene carcinogens.[2,3] In Fig. 1, the monoprotonated derivative of the diamine is shown to have a spectra similar to that of 3-aminodibenzofuran. This means that the 2-amino group in the diamine is the more basic group. This is not unexpected, for the resonance effect of the oxygen atom would have a base-strengthening effect on this group. Consistent with this is the fact that 3-aminodibenzofuran has a pK_a of 3.3 while the diamine has a pK_a of 4.1. The diprotonated derivative of 2,3-diaminodibenzofuran, Fig. 2, curve 1, and the protonated derivative of 3-aminodibenzofuran, Fig. 3, curve 1, are shown to be spectrally similar to dibenzofuran, Fig. 2, curve 2. Comparison of these spectra with that of the diamine in Fig. 3, curve 2, emphasizes the remarkable changes caused by salt formation. In Fig. 4 are

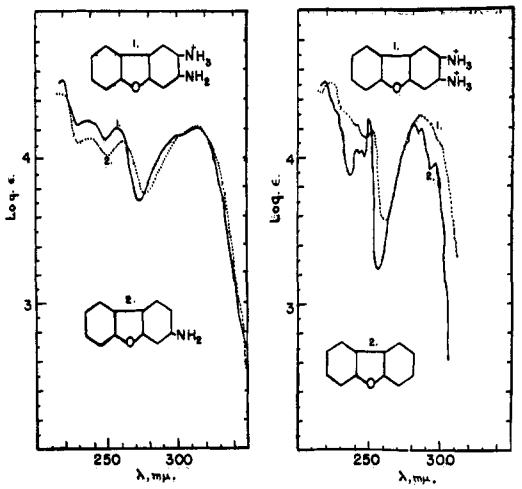

Fig. 1.—(1) 2,3-Diaminodibenzofuran in 50% ethanolic 0.08 N HCl; (2) 3-aminodibenzofuran in 95% ethanol.
Fig. 2.—(1) 2,3-Diaminodibenzofuran in 50% ethanolic 6 N HCl; (2) dibenzofuran in 95% ethanol.

shown the typical curves obtained in the determination of the dissociation constant.

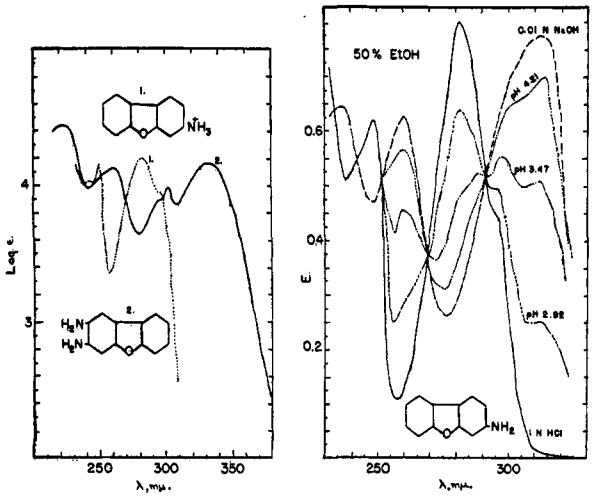

Fig. 3.—(1) 3-Aminodibenzofuran in 50% ethanolic 1 N HCl; (2) 2,3-diaminodibenzofuran in 95% ethanol.
Fig. 4.—3-Aminodibenzofuran in 50% ethanol.

Experimental

Dibenzofuran, m.p. 83–84°, gave an ultraviolet spectrum showing λ_{max} 218, 241, 244, 249, 280, 286 and 296 mμ and log ε 4.51, 4.04, 4.04, 4.26, 4.22, 4.19 and 3.95, respectively. Shoulders occurred at *ca.* 227, 275 and 300 mμ and log ε 4.31, 4.09 and 3.65. This agrees substantially with values reported in the literature.[4]

3-Aminodibenzofuran, m.p. 99°, was prepared by the procedure of Gilman and Avakian.[5] The ultraviolet spectrum showed λ_{max} 217–218, 237–238, 261 and 313 mμ and log ε 4.44, 4.13, 4.11 and 4.22, respectively. A shoulder occurred at 302–303 mμ and log ε 4.15.

2,3-Diaminodibenzofuran, m.p. 166°, was prepared by the procedure of Gilman, *et al.*[6] The ultraviolet spectrum showed λ_{max} 222–223, 259, 302 and 333 mμ and log ε 4.44, 4.12, 3.99 and 4.16, respectively. A shoulder occurred at 295–296 mμ and log ε 3.90.

(1) This investigation was supported by research grant C-1308 from the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service.

(2) E. Miller, J. Miller, R. Sandin and R. Brown, *Cancer Research*, **9**, 504 (1949).

(3) J. A. Miller, E. C. Miller, R. B. Sandin and H. P. Rusch, *ibid.*, **12**, 283 (1952).

(4) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, Curve No. 337.

(5) H. Gilman and S. Avakian, THIS JOURNAL, **68**, 580 (1946).

(6) H. Gilman, G. E. Brown, W. G. Bywater and W. H. Kirkpatrick, *ibid.*, **56**, 2473 (1934).

Procedure.—All absorption spectra were measured by means of a Beckman model DU spectrophotometer and 1-cm. silica cells at 26 ± 1°. In the determination of the ionization constants the spectra of buffered solutions were measured in "50%" aqueous ethanol (100 ml. of the solution contained 50 ml. of water; remainder of the solution consisted of 95% ethanol). The concentration of all compounds was 5×10^{-5} M. The ionization constants were calculated[7] by the equation $pK_a = pH_m + \log (E_B - E_m/E_m - E_{BH^+})$ where E_B, E_{BH^+} are the optical densities of base and salt and E_m is the optical density of a mixture of base and salt at an intermediate pH_m fairly close to the value of the pK_a of the compound.

(7) L. A. Flexser, L. P. Hammett and A. Dingwall, THIS JOURNAL, **57**, 2106 (1935).

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The Preparation of S-Succinyl Coenzyme A[1]

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We have previously concluded that a succinyl derivative is a precursor of protoporphyrin.[3] This succinyl intermediate may be identical with S-succinylcoenzyme A. We have found that this compound is readily formed by succinylating coenzyme A with succinic anhydride, as shown by the disappearance of the sulfhydryl group (nitroprusside reaction),[4] the formation of a hydroxamic acid,[5] and an increased light absorption of 232 mμ.[6] When the product is warmed for a few minutes on a steam-bath, the sulfhydryl group reappears, the reaction with hydroxylamine no longer occurs and there is a decreased light absorption at 232 mμ. Also, this synthetic preparation behaved as succinyl-coenzyme A in enzymatic systems.[7]

Thirty-five mg. of a coenzyme A preparation (Pabst) was dissolved in 30 ml. of ice cold water. To this solution 3 mg. of succinic anhydride was added, followed by sodium bicarbonate until the pH was 7–7.5. The mixture was kept in an ice-bath and shaken frequently. The reaction appeared to be completed within 30 minutes at which time over 90% of the sulfhydryl groups had disappeared. At 0° the succinyl coenzyme A is stable at pH 7–7.5 for several hours, at room temperature it is half hydrolyzed in about 1–2 hours, as measured by the nitroprusside and hydroxamic acid methods. However, at pH 1, at room temperature, the succinyl coenzyme is much more stable than at neutrality. The hydroxamic acid test was carried out on the formed succinyl coenzyme A after the complete hydrolysis of any unreacted succinic anhydride.

Succinyl coenzyme A has previously been enzymatically prepared from α-ketoglutarate.[8,9] Acetic anhydride has been used for the synthesis of acetyl-coenzyme A.[10] This anhydride method may be applicable for the preparation of other acyl coenzyme A derivatives.

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(3) (a) D. Shemin and J. Wittenberg, *J. Biol. Chem.*, **192**, 315 (1951); (b) D. Shemin and S. Kumin, *ibid.*, **198**, 827 (1952).

(4) R. R. Grunert and P. H. Phillips, *Arch. Biochem.*, **30**, 217 (1951).

(5) F. Lipmann and L. C. Tuttle, *J. Biol. Chem.*, **159**, 21 (1945).

(6) E. R. Stadtman, 122d Meeting, Am. Chem. Soc., Atlantic City, N. J., Sept 1952, Abs. 32C.

(7) We are indebted to S. Kaufman, C. Gilvarg, M. J. Coon and J. R. Stern for these enzymatic experiments.

(8) D. R. Sanadi and J. W. Littlefield, *Science*, **116**, 327 (1952).

(9) H. Beinert, 122d Meeting, Am. Chem. Soc., Atlantic City, N. J., Sept. 1952, Abs. 34C.

(10) I. B. Wilson, THIS JOURNAL, **74**, 3205 (1952).

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On Some Partial Molal Volumes of Gases in Solution[1]

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This note reports measurements of the partial molal volumes of carbon tetrafluoride and methane in some non-polar solvents at 27.0°.

Carbon tetrafluoride, obtained from the Minnesota Mining and Manufacturing Company, was led through a Dry Ice trap. Methane, Research Grade from the Phillips Petroleum Company, had been analyzed by mass spectrometer as 99.7% pure. Benzene was obtained thiophene-free or was freed of thiophene by washing with sulfuric acid, sodium carbonate and water, and dried over calcium chloride. Reagent grade (A.C.S.) carbon tetrachloride was used without further purification. *n*-Hexane, *n*-heptane and "isooctane" (2,2,4-trimethylpentane) from the Phillips Petroleum Company were all of 99 mole per cent. purity.

The apparatus and procedure were essentially the same as those of Horiuti[3] and of Gjaldbaek and Hildebrand.[4] The volume of the bulb was approximately 150 cc. The capillary stems had a capacity of about 8.5 cu. mm. per cm. Two dilatometers were used during each run; gas was dissolved in one and the other was used as a blank to correct for small temperature variations in the bath. Compression of the solution by the increased head of mercury in the capillaries was avoided by pulling a sufficient vacuum in one capillary to return the mercury in the other capillary to its original height.

To check the procedure against that of Horiuti and of Gjalbaek and Hildebrand the partial molal volume of methane in benzene was determined at 25.0°. Values of 53.51 and 51.22 cc. per mole were found, which agree well with Horiuti's value of 52.0 and Gjaldbaek and Hildebrand's value of 52.5 cc. per mole. The results of the measurements are summarized in Table I. It will be noted that the value determined for methane in *n*-hexane at 27° differs considerably from the value of 60.0 cc. per mole at 25° found by Gjaldbaek and Hildebrand and that it does not vary in the direction to be expected from the two-degree temperature difference. Horiuti found that the partial molal volume of methane in carbon tetrachloride increased 6.8% in going from 0 to 25°.

As shown by Gjaldbaek and Hildebrand, the partial molal volumes of methane, ethane and nitrogen decrease consistently with increasing solubility parameter of the solvent except for solutions in carbon disulfide. This exception they attribute to the effect of differences in the size and shape of the component molecules. However, if the data for these gases, as given here and in

(1) This note is based on the Master's Thesis of R. H. Schumm, 1952.

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(3) J. Horiuti, *Sci. Papers, Inst. Phys. Chem. Res., Tokyo*, **17**, 125 (1931).

(4) J. Chr. Gjaldbaek and J. H. Hildebrand, THIS JOURNAL, **72**, 1077 (1950).