was connected to a manometric system which included an acetylene reservoir. Pressures, read by means of a cathetometer to ±0.05 mm., were reduced to standard barometric conditions. Temperature was established with a mercury thermometer which had been calibrated by the National Bureau of Standards and could be read to ±0.05°. The powdered sample was outgassed *in situ* under moderate vacuum at 100°. After adjusting the bath to the desired temperature, equilibration took place in from 1 to 3 hours.

The results are shown in Fig. 1. The point represented as a solid circle was approached from both the high and low pressure side, the two readings agreeing to within 1%. All other points were approached from the low pressure side. The dissociation pressures are given by

$$\log_{10} P = 8.538 - 2749/T \qquad (2)$$

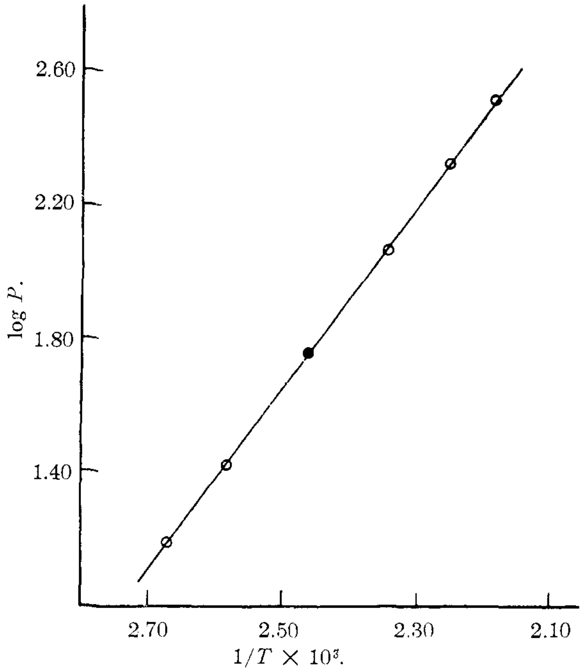

Fig. 1.—Equilibrium pressures (mm.) of acetylene over sodium acetylide and carbides.

The heat of dissociation derived from equation 2 is +12.6 kcal. The heat of dissociation computed from standard heats of formation[4] of the reactants and products at 18° is

$$\begin{array}{cccc} 2\mathrm{NaC_2H} \rightleftarrows & \mathrm{Na_2C_2} + & \mathrm{C_2H_2} & \Delta(\Delta H^\circ) \\ 2(25.1) & (4.1) & (54.3) & 8.2\ \text{kcal.} \end{array}$$

The standard heats of formation of the solids are derived from measurements of heats of solution.

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(4) F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publ. Corp., New York, N. Y., 1936, pp. 144–145; P. W. Wagman, J. E. Kilpatrick, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 467 (1945).

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The System of *p*- and *o*-Ethylacetanilides

BY GENNADY M. KOSOLAPOFF

RECEIVED JUNE 6, 1955

Probably the most convenient route to many of the derivatives of ethylbenzene lies through the intermediates of *o*- and *p*-nitroethylbenzenes and the corresponding amines. The acetyl derivatives of the latter afford a convenient check on the purity of the isomers, and the quality of the subsequent products. However, the existing data in the literature concerning these acetyl derivatives must be regarded as extremely scanty, since only the individual melting points are recorded[1–3] and no quantitative data may be found about their solubilities.

It was felt that the determination of the phase diagram of the two acetyl derivatives and the determination of their solubilities in water would be of assistance in filling this informational gap.

The necessary nitro and amino compounds were prepared in a manner similar to that employed by Birch, *et al.*[1] However, it was observed that if the crude nitroethylbenzenes are steam distilled, prior to the vacuum fractionation, no difficulty in respect to decomposition is observed even if the pot temperature is maintained at well above 150° for many hours (usually 24–30 hours) during the fractionation. The amines were acetylated conventionally with acetic anhydride in sodium acetate buffer and the substances were recrystallized: the *ortho* isomer from water, the *para*-isomer from dilute alcohol.

While the method of cooling curves gave good results with the pure substances and with their mixtures at the extremities of the composition curve, it was unsatisfactory in the mid-portion of the diagram owing to very severe supercooling and glass formation. For this reason, the phase diagram of *o*- and *p*-ethylacetanilides was explored by the method of capillary melting points, only the pure isomers and their 10:90 mole % mixtures being further verified by the cooling curve method.[4]

The phase diagram of the system is that of solid solution type with a eutectic as shown in Table I. The temperatures given are corrected.

Solubilities of the two isomers in distilled water were determined at 30° and at 50°. It is to be noted that the *p*-isomer shows a decidedly higher temperature coefficient of solubility than does the *o*-isomer. The determinations were made conventionally by equilibration of the powdered solids

TABLE I

THE SYSTEM OF *o*- AND *p*-ETHYLACETANILIDES

o-Isomer, mole %	Liquidus, C.	Solidus, C.	*o*-Isomer, mole %	Liquidus, C.	Solidus, C.	Solubility, g./100 ml. soln.	
						o-Isomer	*p*-Isomer
						30°	
100	112.9	112.9	40	67.5	65.0	0.4192	0.1168
90	109.5	95.0	30	74.0	67.4		
80	104.8	84.0	20	84.0	74.0	50°	
70	97.8	75.0	10	90.5	82.5	.5256	.2276
60	89.0	69.5	0	94.8	94.8		
50	79.2	66.0	38.8	64.8	64.5		

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(1) S. F. Birch, R. A. Dean, F. A. Fidler and R. A. Lowry, THIS JOURNAL, **71**, 1362 (1949).

(2) W. J. Hickinbottom, *J. Chem. Soc.*, 64 (1927).

(3) J. v. Braun, O. Bayer and G. Blessing, *Ber.*, **57**, 398 (1924).

(4) In the determination of the final melting temperatures (liquidus line) it was convenient to observe the appearance of the reflection of the translucent specimen in the capillary as it appeared on the mercury bulb of the thermometer, the incident light being directed through the specimen. The instant of disappearance of the trace of haze was much more readily observable in this manner than it was by direct observation of the specimen.

with water with agitation in a thermostat. The results are given in Table I.

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The Titration of Polyamines in the Presence of Sodium Dodecyl Sulfate[1]

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RECEIVED MAY 18, 1955

In studies of competitive equilibria between proteins and polyamines for metal ions, it became necessary to evaluate the purity of a number of these polybases. For this purpose, the titration procedure of Gause, Crumpler and Jonassen[2] was followed. In essence their method consists of plotting the derivative of the titration curve, $\Delta(p\mathrm{H})/\Delta V$, against V, the volume of added standard acid, and observing whether the peaks occur at the proper mole ratios. With tetraethylenepentamine, for example, these investigators[2] felt that end-points for four of the five protons taken up by the base could be observed readily.

In our experience we felt very uncertain about the exact position of most of the end-points. Since a small error in this reading becomes greatly magnified in calculations of per cent. purity, we searched about for a method of sharpening the titration curve.

A suitable method suggests itself on consideration of the fundamental reason for the shallow slopes in the titration curve in the first place. Ordinarily the pK_a of an amine in aqueous solution lies near 10 so that titration with nitric acid gives a sharp end-point. With several basic nitrogen groups on the same molecule, however, each added proton magnifies the electrostatic repulsion toward subsequent protons and hence pK_a's are lowered greatly. To overcome this electrostatic repulsion, it seemed appropriate therefore to add a large organic anion to the solution so that as the polyammonium ion is formed, repulsion of successive protons would be minimized by formation of an anion-cation complex.

In practice sodium dodecyl sulfate proved to be eminently suitable. Titration curves were greatly sharpened with triethylenetetramine,[3] tetraethylenepentamine and the hexamine[3] N,N,N',N'-(β-aminoethyl)-ethylenediamine, respectively (Fig. 1). It seems, therefore, that this procedure should be applicable generally in examinations of the stoichiometry of acid titrations of polyamines.

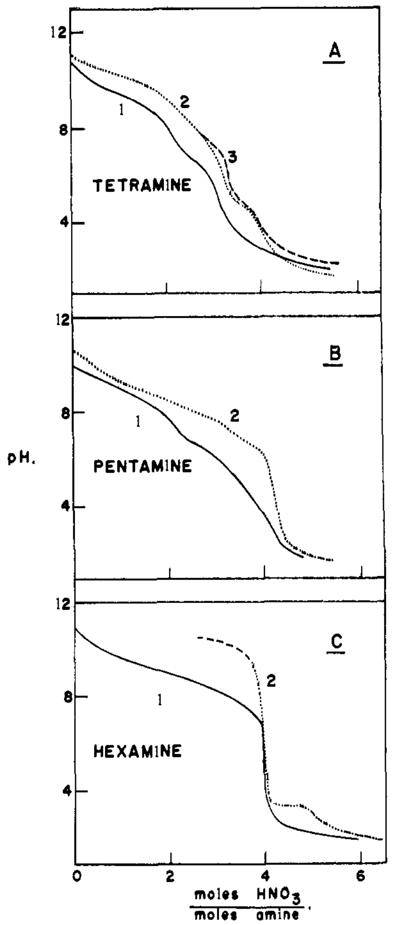

Fig. 1.—A, titration of triethylenetetramine in aqueous solution: 1, 0.198×10^{-3} mole tetramine in water; 2, 0.198×10^{-3} mole tetramine with 2.06×10^{-3} mole sodium dodecyl sulfate (U.S.P.); 3, 0.111×10^{-3} mole tetramine with 2.24×10^{-3} mole sodium dodecyl sulfate (crystalline) (curves 1 and 2 in nitrogen atmosphere).

B, titration of tetraethylenepentamine: 1, 0.335×10^{-3} mole pentamine; 2, 0.335×10^{-3} mole pentamine with 1.66×10^{-3} mole sodium dodecyl sulfate (crystalline).

C, titration of N,N,N',N'-(β-aminoethyl)-ethylenediamine (hexamine): 1, 0.129×10^{-3} mole hexamine; 2, 0.129×10^{-3} mole hexamine with 0.878×10^{-3} mole sodium dodecyl sulfate (crystalline).

Experimental

A commercial grade of triethylenetetramine was used as received. Tetraethylenepentamine was fractionated by the ion exchange method of Gause, Crumpler and Jonassen.[2] The hexamine, N,N,N',N'-(β-aminoethyl)-ethylenediamine was a research sample of high purity.[6] Purified sodium dodecyl sulfate was a product of E. I. du Pont de Nemours and Company. A U.S.P. grade of sodium dodecyl sulfate also was used.

Titrations were carried out with a Beckman Model G pH meter using external electrodes. Triethylenetetramine was titrated in an atmosphere of nitrogen as well as in air.

In each titration with dodecyl sulfate an insoluble anion-cation complex was formed ultimately. The formation of this complex produced drifts upward in pH, probably due to slow diffusion of protons into the insoluble complex. Continuous stirring resulted in reproducible readings.

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(1) This work was carried out during the tenure (1952–1953) of a Public Health Service post-doctorate research fellowship, from the National Institute of Neurological Diseases and Blindness.

(1a) National Institute of Neurological Diseases and Blindness, Bethesda 14, Maryland.

(2) E. H. Gause, T. B. Crumpler and H. B. Jonassen, THIS JOURNAL, **73**, 5457 (1951).

(3) Only in the presence of dodecyl sulfate could the uptake of the fourth proton by triethylenetetramine, and of the fifth proton by hexamine, be observed distinctly. Pentamine evidently does not form a pentammonium complex and hexamine does not form a hexammonium complex.[4]

(4) G. Schwarzenbach and P. Moser, *Helv. Chim. Acta*, **36**, 581 (1953).

(6) We are indebted to Dr. W. Gauss of the Leverkusen Works of I. G. Farbenindustrie for a gift of this material.