bromoaniline, a good yield of 2,6-dibromoaniline should be obtained. However, it was found that a mixture of dibromo- and tribromoaniline resulted from the desulfonamidation. Thus, the formation of an N^1-bromo sulfonamide does not appear to be a necessary intermediate in the formation of the *tri*bromo aniline from the *di*bromo sulfanilamide.[2]

Experimental[3]

N^1,N^1-Diethyl-3,5-dibromosulfanilamide.—N^1,N^1-Diethylsulfanilamide[4] (25 g.) was dissolved in 250 cc. of glacial acetic acid. Bromine (44 g.) dissolved in 175 cc. of glacial acetic acid was added dropwise with stirring; after all of the bromine had been added, the mixture was allowed to stand at room temperature for two minutes and then diluted with ice water. The precipitate was collected, thoroughly washed with water and dried. The crude product weighed 37 g. (87%), m. p. 175–178°. Three recrystallizations from ethanol gave clusters of very short needles, m. p. 181.5–182.5°.

Anal.[5] Calcd. for $C_{10}H_{14}O_2Br_2N_2S$: N, 7.26. Found: N, 7.32.

Desulfonamidation of N^{1}N^1-Diethyl-3,5-dibromosulfanilamide.—The sulfanilamide (20 g.) was refluxed with 100 ml. of 70% sulfuric acid for three hours. At the end of that time the reaction mixture was cooled and poured into ice water. A white precipitate was obtained (6 g.), m. p. 114–116°. Recrystallization from ethanol raised the m. p. to 116–118°. The mixed m. p. with an authentic sample of 2,4,6-tribromoaniline (m. p. 120–121°) was 115.5–118°.

The filtrate remaining after the removal of the tribromoaniline was steam distilled to yield 2 g. of somewhat impure 2,6-dibromoaniline, m. p. 75–77°. The melting point could not be improved by crystallization, in agreement with the observation of other workers.[1] The material could be easily converted to pure 2,4,6-tribromoaniline with the use of bromine water.

The residue remaining after the steam distillation was made basic with alkali and extracted with ether. The ether was evaporated and a small amount of dark brown oil remained. This could be converted to 2,4,6-tribromoaniline (m. p. 120–121°); mixed m. p. with an authentic sample was not depressed.

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(2) Disproportionations of halo anilines have been reported previously in the literature. *E. g.*, Wheeler and Liddle, *Am. Chem. J.*, **42**, 453 (1909), found that a mixture of 3,5-diiodobenzoic and *p*-aminobenzoic acids resulted from acid hydrolysis of 3-iodo-4-acetamidobenzoic acid, although the formation of an N-halo acetamide could not be ruled out as a necessary intermediate in this disproportionation. Distillation of *p*-bromoaniline yields tribromoaniline (Fittig and Buchner, *Ann.*, **188**, 23 (1877)). This reaction, being pyrolytic in nature, may well proceed by a different mechanism from the examples mentioned above.

(3) Melting points are uncorrected.

(4) Gray, Buttle and Stephenson, *Biochem. J.*, **31**, 724 (1937).

(5) We are indebted to Mrs. Joan Buck for the analysis.

DEPARTMENT OF CHEMISTRY
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On the Indicator Acidity Function H_0 and the Acid-catalyzed Decomposition of Trioxane

BY MARTIN A. PAUL

The reaction rates reported by Walker and Chadwick[1] for the acid-catalyzed decomposition of trioxane, the cyclic trimer of formaldehyde, may be nicely correlated with the H_0 acidity function defined by Hammett and Deyrup.[2] Figure 1 shows the logarithm of the first-order rate constant plotted against H_0 for solutions of sulfuric acid in water, hydrochloric acid in water, and sulfuric acid in glacial acetic acid. The reaction rates are at 40° while H_0 is at 25°, but there appears to be no reason to expect a radical change in the H_0 scale with temperature. As a matter of fact, Walker and Chadwick report rate data at other temperatures, but the series at 40° is the most complete.

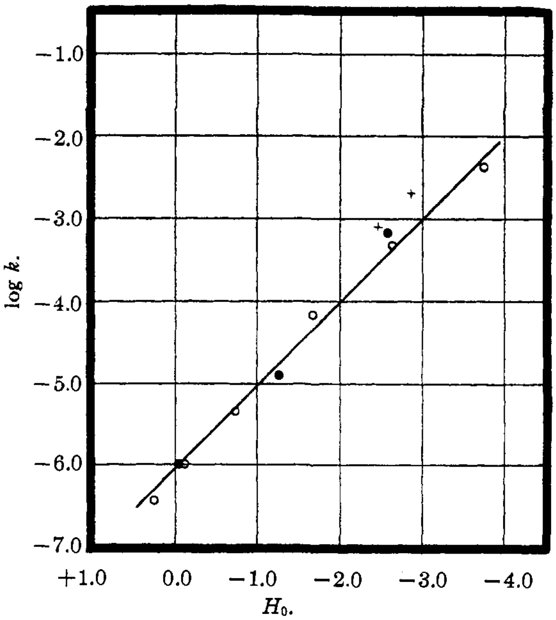

Fig. 1.—Log *k vs.* H_0 for the acid-catalyzed decomposition of trioxane: ○, H_2SO_4 in water; ●, HCl in water; +, H_2SO_4 in glacial acetic acid.

The concentrations of sulfuric acid in water cover a range from 0.5 to 8 *M*, involving a 10,000-fold change in the rate constant, and over this range, log *k* appears to be a linear function of H_0 with slope 1. The H_0 value for the highest hydrochloric acid concentration (7.75 *M*) should not be given too much weight, as it was obtained by extrapolation from the data of Hammett and Paul,[2] which extend only to 6 *M*. It is significant, however, that the H_0 plot brings aqueous sulfuric acid and aqueous hydrochloric acid into agreement, for Walker and Chadwick noted that in terms of the acid *normality*, hydrochloric acid appeared to be a relatively better catalyst than sulfuric acid. Secondary ionization of sulfuric acid is of course quite minor in effect at concentrations exceeding 1 *M*.[3]

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(1) J. F. Walker and A. F. Chadwick, *Ind. Eng. Chem.*, **39**, 974 (1947).

(2) L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2721 (1932); L. P. Hammett and M. A. Paul, *ibid.*, **56**, 827, 830 (1934); L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 262 et seq.

(3) M. S. Sherrill and A. A. Noyes, THIS JOURNAL, **48**, 1861 (1926); W. J. Hamer, *ibid.*, **56**, 860 (1934).

The quite fair agreement of the correlation in the case of solutions of sulfuric acid in glacial acetic acid with that in the aqueous solutions is impressive. The H_0 values for these superacid solutions are taken from work of Paul and Hammett, which is in agreement with the more extensive work of Hall and Spengeman.[4] One should note that both H_0 and the rate constant for the reaction are about the same in 1 M sulfuric acid solution in glacial acetic acid as in 6.5 M aqueous solution. This appears to be the first correlation found between a reaction rate and H_0 in glacial acetic acid.[5] The apparent simplicity of the reaction from the experimental point of view and its conveniently measurable rate in quite strongly acid solutions suggest further applications to the study of acid catalysis mechanisms, some of which are being explored at this Laboratory.

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[4] M. A. Paul and L. P. Hammett, THIS JOURNAL, **58**, 2182 (1936); N. F. Hall and W. F. Spengeman, *ibid.*, **62**, 2487 (1940).

[5] For the correlation of a reaction rate with the essentially different potentiometric pH_{HAc} scale of N. F. Hall and J. B. Conant, *ibid.*, **49**, 3047 (1927), see J. B. Conant and G. M. Bramann, *ibid.*, **50**, 2305 (1928).

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Side-Chain Bromination. III. Fluorobenzyl Bromides

BY JOHN R. SAMPEY AND ANNE K. MCCUEN

The photobromination of the fluorotoluenes has not been studied. We found one bromine may be introduced readily into the side-chain under the influence of a strong mercury arc.

Experimental.—The ease of side-chain bromination of the fluorotoluenes was determined by the time required to decolorize the bromine solution. The brominations were carried out on 10-g. samples dissolved in 50 ml. of carbon tetrachloride in a round-bottom Pyrex flask fitted with a reflux condenser and calcium chloride outlet tube. A 6-inch mercury arc was placed 0.75 inch from the flask on a hot water-bath. A molar solution of bromine in carbon tetrachloride was added through a dropping funnel as rapidly as the bromine color faded. At the end of the time indicated the solvent was removed under a vacuum and the residue dried and analyzed for side-chain bromine.[1] *o*-Fluorotoluene gave 69.6% active bromine in four minutes; *m*-F 70.9% in 6 min.; *p*-F 76.5% in 16 min.; several other substituted toluenes were included to correlate the results with a previous study.[2] *o*-Bromotoluene decolorized in twenty minutes to give 69.8% side-chain bromine; *m*-Br 70.8% in six minutes; *p*-Br 87.3% in six minutes; *o*-I 14.4% in ten minutes; *m*-I 44.4% in 120 minutes. (The color of the solution made it difficult to determine how rapidly the bromine reacted); 3,5-dimethyl 89.5% in six minutes.

Samples of the three fluorobenzyl bromides were purified by vacuum distillation and found to correspond with those made from fluorobenzyl alcohols; ortho isomer b. p. 84–86° (15 mm.); meta isomer 73–75° (15 mm.); para isomer 85–87° (15 mm.).[3]

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[1] Sampey, Blitch and King, THIS JOURNAL, **70**, 2606 (1948).

[2] Sampey, Fawcett and Morehead, *ibid.*, **62**, 1839 (1940).

[3] Shoesmith and Slater, *J. Chem. Soc.*, 214–223 (1926).

Limitations of the Anthrone Test for Carbohydrates

BY LOUIS SATTLER AND F. W. ZERBAN

The Dreywood[1] anthrone reagent gives a positive qualitative test for a large variety of carbohydrates and their derivatives, as well as for furfural and 5-hydroxymethylfurfural, but it gives a negative test[2] for D-glucose phenylosazone and D-glucose phenylosotriazole. In view of the fact that a positive test is obtained with D-mannose phenylhydrazone, the writers[2] suggested that the anthrone reaction requires the initial formation of furfural or a derivative of it.

In the mechanism of the formation of 5-hydroxymethylfurfural from sugars, Wolfrom, Schuetz and Cavalieri[3] proved that the first step requires the elimination of a molecule of water between carbons 2 and 3, leaving an OH group on carbon 2. The anthrone test has now been applied to D-glucosone[4] and to 2-desoxyribose[5] and in each case the expected negative test was observed, thus supporting the original postulation for the requirement for a positive test. With 5-desoxy-L-sorbose[6] a non-characteristic tan to lavender color was obtained depending on the sugar concentration.

The writers wish to thank Clarence E. May of Indiana University, John C. Sowden of Washington University and Peter P. Regna of Charles Pfizer and Company, for their kind coöperation.

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[1] Dreywood, *Ind. Eng. Chem.*, *Anal. Ed.*, **18**, 499 (1946).

[2] Sattler and Zerban, *Science*, **108**, 207 (1948).

[3] Wolfrom, Schuetz and Cavalieri, THIS JOURNAL, **70**, 514 (1948).

[4] Becker and May, *ibid.*, **71**, 1491 (1949).

[5] Sowden, *ibid.*, **72**, 808 (1950).

[6] Regna, *ibid.*, **69**, 246 (1947).

BROOKLYN COLLEGE
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A Synthesis of N,N-Diphenylcarbamic Anhydride[1]

BY W. A. SCHROEDER AND PHILIP E. WILCOX

The only reported synthesis of N,N-diphenylcarbamic anhydride is that of Herzog and Budy[2] who prepared it by treating the addition product of pyridine and N,N-diphenylcarbamyl chloride with dilute sodium hydroxide. Since their procedure failed to give satisfactory results, recourse was had to a classical method for the preparation

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[1] This paper is based on work done for the Office of Scientific Research and Development under Contract OEMsr-881 with the California Institute of Technology.

[2] J. Herzog and K. Budy, *Ber.*, **44**, 1584 (1911).