TABLE I
1-NITROSO- AND 1-AMINO-2-HYDROXY-3-NAPHTHOIC ACID ARYL AMIDES

	Condensation product of 2-hydroxy-3-naphthoic acid with	Commercial name, naphthol	1-Nitroso derivative, m. p., °C. (uncor.)	Nitrogen content, % Calcd.	Found	1-Amino derivative, m. p., °C. (uncor.)	Nitrogen content, % Calcd.	Found
1	Aniline	AS	221–222	9.58	9.55	190–192[a]	...	...
2	o-Toluidine	ASD	207–208	9.78	9.60	162–164	9.58	9.38
3	2,4-Dimethylaniline	ASMX	212–213	8.75	8.74	166–168	9.15	9.08
4	o-Anisidine	ASOL	216–217	8.69	8.52	161–163	9.09	8.96
5	p-Anisidine	ASRL	217–218	8.69	8.61	160–162	9.09	8.93
6	o-Phenetidine	ASOP	234–235	8.36	8.35	151–153	8.70	8.44
7	Alpha-naphthylamine	ASBO	236–237	8.19	8.01	201–203	8.54	8.40
8	Beta-naphthylamine	ASSW	222–223	8.19	7.99	184–186	8.54	8.51
9	m-Nitroaniline	ASBS	255–256	12.46	12.25	183–185[b]	14.33	14.24
10	p-Chloroaniline	ASE	241–242	8.57	8.46	160–162	8.96	9.00
11	5-Chloro-o-toluidine	ASTR	221–222	8.22	8.16	182–184	8.58	8.51
12	5-Chloro-2,4-dimethoxyaniline	ASITR	233–234	7.24	7.19	215–217	7.52	7.36

[a] M. p. literature, 188–190°. [b] Diamine formed by reduction of nitro group on condensing amine.

Naphthol AS intermediates, and reducing the resulting nitroso compounds with zinc dust and glacial acetic acid, in a dioxane solvent. Comparison with the amino derivatives of the coupling components from the corresponding Naphthol AS type pigments, disclosed that both were identical.

Experimental

Materials.—The compounds reported in this paper were prepared from commercially available Naphthol AS dyestuff intermediates, which were found to be true to type and sufficiently pure for immediate use.

Preparation of 1-Nitroso-2-hydroxy-3-naphthoic Acid Aryl Amides.—Nitrosation of the aryl amides was achieved in 85–90% yields by the general method described below: One-twentieth gram mole of the amide was suspended in 200 ml. of dioxane, which had been previously cooled to 20° and the mixture was mechanically agitated while 20 ml. of a 25% sodium nitrite solution was added, followed at once by 10 ml. of concd. hydrochloric acid. During the first five minutes, the mixture progressively changed color, sometimes accompanied by solution of the amide. After one hour, the precipitated nitroso derivative was collected on a Buchner funnel, washed with 25 ml. of cold alcohol, and dried. Portions of the yellow to brick-red precipitates were crystallized from dioxane, for purposes of establishing melting point and analytical data, Table I.

Preparation of 1-Amino-2-hydroxy-3-naphthoic Acid Aryl Amides.—Three-gram portions of the crude nitroso were reduced, by refluxing for one hour, with a mixture of 10 g. of zinc dust, 50 ml. of dioxane and 10 ml. of glacial acetic acid. The hot reaction mixture was filtered, to remove insoluble matter, which was then washed with 25 ml. of dioxane, and the filtrate was acidified at once with 50 ml. of hydrochloric acid, to precipitate the amino hydrochloride. After cooling overnight to achieve maximum yield, the solid was collected on a Buchner funnel, washed with a small volume of dioxane and transferred to a 500-ml. extraction funnel with about 50 ml. of alcohol.

The suspended amino hydrochloride was buffered with 10 ml. of a 10% sodium acetate solution, to liberate the free base, and the mixture was diluted with 250 ml. of ether. Any remaining solid was solubilized by the addition of 200 ml. of a 2.5% sodium acetate solution, and the ether layer was then washed several times with water, dried with anhydrous sodium sulfate, filtered and evaporated to near dryness. Resolution of the residue was effected with 50 ml. of hot benzene, and incipient crystallization of the amino-arylamide was attained by dilution with petroleum ether. Yellow to greenish crystals were precipitated, after standing overnight in the refrigerator, and the product was purified from benzene–petroleum ether.

Occasionally, solution of the amino-Naphthol AS com-

pound could not be accomplished with ether. When this occurred, 100 ml. of benzene and 50 ml. of xylene were added to the ether layer, and the mixture was evaporated until only xylene remained. This caused solution of the amino-arylamide, which was then precipitated with petroleum ether, and purified as previously described. Amine yields of 60–85% were obtained.

Acknowledgment.—The authors wish to express their thanks to Mr. W. C. Bainbridge, director of the laboratories, for his interest in this work.

### The Desulfonamidation of N^1,N^1-Diethyl-3,5-dibromosulfanilamide

By CARL M. MOSER AND G. S. MELVILLE, JR.

An N^1-bromo sulfonamide may be a necessary intermediate in the formation of 2,4,6-tribromoaniline from the desulfonamidation of 3,5-dibromosulfanilamide in the usual manner.[1] Displacement of Br+ by a proton from the primarily formed 2,6-dibromoaniline, reaction of this fragment with the dibromo sulfanilamide to form the N^1-halo compound, and bromination of the dibromo aniline with the latter compound would complete the sequence of the steps in the mechanism.

In order to test this hypothesis N^1,N^1-diethyl-3,5-dibromosulfanilamide was prepared and sub-

$$H_2N-\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle Br}{|}}{\bigcirc}}-SO_2N(C_2H_5)_2$$
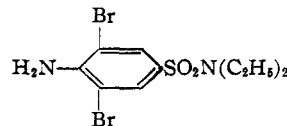
jected to desulfonamidation by refluxing a solution of the sulfanilamide in 70% sulfuric acid. The formation of an N^1-bromosulfonamide is not possible here, and, if such a compound is a necessary intermediate in the formation of 2,4,6-tri-

(1) The report of Fuchs, *Monatsh.*, **36**, 124 (1915), that only 2,6-dibromoaniline is formed in this reaction could not be confirmed; *cf.* Seikel, *Organic Syntheses*, **24**, 47 (1944).

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^1N^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.

(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
THE JOHNS HOPKINS UNIVERSITY
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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,

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

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.
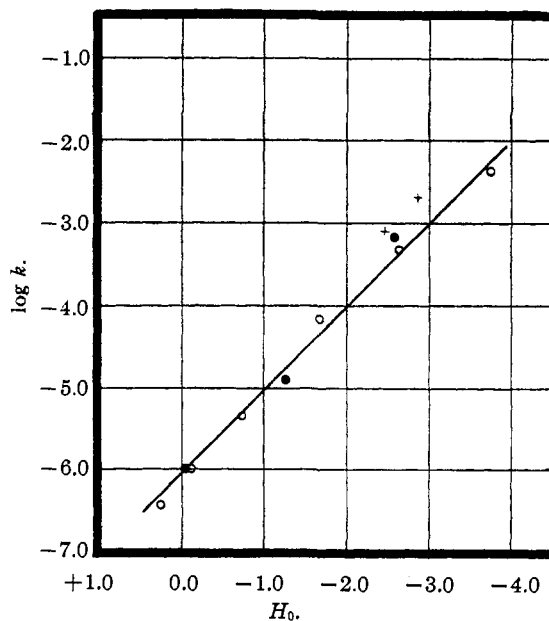

Fig. 1.—Log k vs. H_0 for the acid-catalyzed decomposition of trioxane: O, H_2SO_4 in water; ●, HCl in water; +, H_2SO_4 in glacial acetic acid.

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]

(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).