σ-1-Amino-4-di-*n*-propylaminobenzene Bromide.—Oxidation in this and the following two experiments were conducted as in the example above. Quantities of reagents and degree of temperature were kept constant and only the amount of the amine varied. In this case 9.6 g. of di-*n*-propylaniline was treated; yield 6.2 g. of brilliant green micro crystals. The product in water gives a bright bluish-red solution; m. p. turns brown at 100°, and melts from 190–195° uncor. *Anal.* Calcd. $C_{12}H_{20}N_2Br$: Br, 29.36. Found: Br, 28.80.

σ-1-Amino-4-di-*n*-butylaminobenzene Bromide.—Eleven grams of di-*n*-butylaniline was oxidized to give 9.2 g. of brilliant green crystals. Solution is similar to the dipropyl compound; m. p. 111–119° uncor. *Anal.* Calcd. $C_{14}H_{24}N_2Br$: Br, 26.61. Found: Br, 26.60.

σ-1-Amino-4-morpholinebenzene Bromide.—From 8.9 g. of *p*-aminophenylmorpholine, after oxidation with the bromine solution, 8 g. of deep olive green crystals was obtained which gave a deep purple-red solution in water, m. p. 130° uncor. *Anal.* Calcd. $C_{10}H_{14}ON_2Br$: Br, 30.95. Found: Br, 31.20.

σ-1,4-Bis-(dimorpholine)-benzene Bromide.—To 12.4 g. of 1,4-phenylenedimorpholine dissolved in 160 cc. of dioxane + 80 cc. of acetic acid and cooled to 30°, a mixture of 1.2 cc. of bromine in 80 cc. of dioxane + 24 cc. of acetic acid was added dropwise. A slate gray precipitate formed which when dried weighed 14 g. and gave an intense blue-violet solution in water; m. p. 266°, uncor. *Anal.* Calcd. $C_{14}H_{20}O_2N_2Br$: Br, 24.35. Found: Br, 24.15.

σ-4,4′-Diaminodiphenyl Bromide.—In a mixture of 50 cc. of dioxane + 40 cc. of acetic acid 4.6 g. of benzidine was dissolved and cooled to 5°. Six-tenths cc. of bromine in 40 cc. of dioxane + 12 cc. of acetic acid were added over one-half hour and the dark blue precipitate collected at once. After washing with 200 cc. of ether the solid was dried *in vacuo* and weighed 4.75 g. The dried material was dark green and gave a blue solution in water; m. p. turns gray at 160° and does not melt below 300°. *Anal.* Calcd. $C_{12}H_{12}N_2Br$: Br, 30.25. Found: Br, 30.64.

σ-3,3′-Dimethoxy-4,4′-diaminodiphenyl Bromide.—Six and one-tenth grams of dianisidine was dissolved in 80 cc. of dioxane + 40 cc. of acetic acid, cooled to 0°, and treated with a mixture of 0.6 cc. of bromine dissolved in 40 cc. of dioxane + 12 cc. of acetic acid. After standing one hour the blue-green precipitate was collected, washed with 200 cc. of ether and dried *in vacuo;* yield 6.6 g. In water the compound gives a blue-green solution; m. p. turns gray above 140° and melts at 254°. *Anal.* Calcd. $C_{14}H_{16}O_2N_2Br$: Br, 24.65. Found: Br, 24.33.

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The Properties of Hydroxylamine. I. The Reduction of Hydroxylammonium Salts by Arsenite

BY KELSO B. MORRIS, DAVID F. JOHNSON[1] AND JOSEPH B. MORRIS[2]

In an effort to extend the work of Gutman[3] on the reaction between salts of hydroxylamine and sodium arsenite, data have been obtained for (1) decomposition of hydroxylammonium salts in the presence of sodium hydroxide and (2) reduction of hydroxylammonium salts by arsenite.

Experimental

From 10 to 15 ml. of water was added to a definite amount of hydroxylammonium salt present in the Kjeldahl flask of an ammonia distillation apparatus. Forty-five ml. of the sodium hydroxide solution, which did or did not contain primary-standard quality arsenic(III) oxide, was then added to the fairly concentrated salt solution. Gradual mixing of the solutions was effected, after which the ammonia formed was distilled over into excess standard acid in the usual manner. Residual solutions were all diluted to one-liter volumes and separate series of aliquots analyzed for arsenite and arsenate. Arsenite, in a medium properly buffered with sodium bicarbonate, was determined by titration with standard iodine solution. For the determination of arsenate, iodate-free potassium iodide was added to aliquots made highly acidic with sulfuric acid. The iodine liberated was titrated with sodium thiosulfate. Unreacted hydroxylamine was never found, after distillation, in either the reaction flask or in the receiver.

TABLE I

DECOMPOSITION OF HYDROXYLAMMONIUM SALTS IN THE PRESENCE OF SODIUM HYDROXIDE

Salt, g. $NH_2OH \cdot HCl$	Salt, millimoles	% NaOH, 45 ml.	Total NH_3 absorbed, millimoles	Ratio, total NH_3/salt, millimoles
1.4848	21.362	15	7.189	0.337
1.5112	21.740	15	7.472	.344
1.4546	20.927	15	7.017	.335
			Av.	.339
1.3150	18.920	30	6.492	.343
1.6604	23.888	30	7.889	.330
1.5192	21.857	30	7.543	.344
			Av.	.339
$NH_2OH \cdot {}^1/_2H_2SO_4$				
3.0498	37.962	15	10.951	.295
2.8304	34.432	15	10.157	.295
2.3462	28.540	15	8.122	.284
			Av.	.291
2.3079	28.066	30	9.797	.349
2.4712	30.064	30	10.112	.336
2.3482	28.566	30	9.802	.343
			Av.	.343

Hydroxylamine decomposes, in alkaline solution, according to the equation

$$3NH_2OH \longrightarrow NH_3 + 3H_2O + N_2 \qquad (1)$$

The data of Table I indicate that the amounts of ammonia resulting from the decomposition of the chloride and sulfate salts of hydroxylamine are essentially the same for 15 and 30% sodium hydroxide. Too, three moles of salt produce one mole of ammonia in accordance with (1). The yield of ammonia from the sulfate salt with 15% sodium hydroxide differs from the other data by about twelve per cent. despite the fact that the concentration of alkali in the final mixture is the same as for the chloride salt. A discrepancy of this sort is not uncommon for reactions of hydroxylammonium salts which are not carried out

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[1] Reported at the meeting of the Washington Section of the American Chemical Society, November 10, 1949.

[2] A part of the work reported herein was done under a contract between the Office of Naval Research and Howard University.

[3] A. Gutman, *Ber.*, **55B**, 3010 (1922).

TABLE II

REDUCTION OF HYDROXYLAMMONIUM SALTS BY ARSENITE

Salt, g. $NH_2OH \cdot HCl$	Salt, millimoles	% NaOH, 45 ml.	As_2O_3, millimoles	Total NH_3 absorbed, millimoles	Ratio total NH_3/salt, millimoles	Ratio, total NH_3/AsO_2^- reacted, millimoles
1.5046	21.642	15	24.687	9.398	0.434	1.247
1.5600	22.444	15	24.255	9.664	.431	1.287
1.3453	19.365	15	24.456	8.382	.433	1.421
				Av.	.439	1.318
1.3922	20.030	30	25.357	8.826	.441	3.219
1.4794	21.286	30	24.407	9.353	.440	3.188
1.4739	21.204	30	24.572	9.274	.437	3.272
				Av.	.440	3.226
$NH_2OH \cdot {}^1/_2H_2SO_4$						
1.9737	24.002	15	25.029	9.291	.389	0.977
1.9493	23.712	15	24.913	9.087	.383	1.130
2.0244	24.626	15	24.841	9.775	.396	1.152
				Av.	.389	1.086
1.7514	21.304	30	24.565	9.318	.437	2.829
1.7789	21.640	30	24.746	9.469	.438	2.917
1.7296	21.040	30	25.435	9.280	.441	2.822
				Av.	.439	2.856

under *precisely-controlled* conditions. According to the present work, the suggestion of Michael,[4] that explosive sodium hydroxylamite must exist under conditions such as employed in the present work, appears highly unlikely.

When arsenite is present, a second reaction is involved, *viz.*, reduction of hydroxylamine by arsenite. This reaction is possibly

$$2OH^- + AsO_2^- + NH_2OH \rightleftarrows AsO_4^{-3} + NH_3 + H_2O \quad (2)$$

for which the calculated equilibrium constant is $K = 10^{37.6}$. Table II shows a higher ratio, total NH_3/salt, than in Table I where arsenite is not present. For 30% solutions, there is a decrease in the amount of arsenite reacting (increase in ratio, total NH_3/AsO_2^- reacted). To account for this fact, it is postulated that the increase in rate of (1) may be due to the high concentration of alkali and/or catalysis of this decomposition reaction, presumably by arsenite.

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[4] A. Michael, THIS JOURNAL, **43**, 315-332 (1921).

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The Reaction of 2,5-Dihydroxyquinone with Thorium Ion in Methanol Solution

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It has been shown[2] that in aqueous solution 2,5-dihydroxyquinone precipitates thorium ion as a purple compound containing two moles of the quinone to one of thorium. When very dilute thorium salt solutions (0.006 *M* or less) are treated with the ammonium salt of 2,5-dihydroxyquinone (0.01 *M* or less), however, purple solutions result. Unfortunately, these solutions deposit precipitates within a few minutes, especially as the concentrations of the reagents increase to the above limits, and are too unstable to be studied in detail or to be useful for analytical purposes. Variation in *p*H between 3.4 and 5.0 has no effect. At lower *p*H values, the quinone itself precipitates, while at higher *p*H values, the precipitate is largely hydrous thorium oxide.

In methanol, thorium ion and 2,5-dihydroxyquinone react to give purple solutions which precipitate only after standing for several hours. Because of the potential applicability of this color reaction to the determination of thorium, it was of interest to determine the composition of the colored species in such solutions. This was done by Job's method of continuous variations[3] as modified by Vosburgh and Cooper,[4] using absorption spectra measurements.

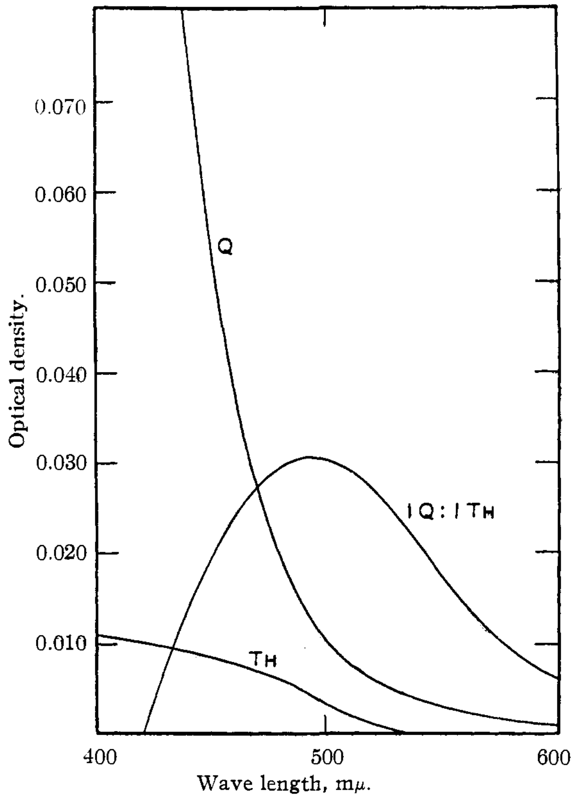

Fig. 1.—Absorption spectra of 2,5-dihydroxyquinone (Q), thorium nitrate (Th), and an equimolar mixture of the two (1 Q:1 Th) in methanol.

In Fig. 1, the absorption spectra of 0.001 *M* 2,5-dihydroxyquinone (Q), 0.001 *M* thorium nitrate (Th) and a mixture of equal volumes of 0.001 *M* 2,5-dihydroxyquinone and 0.001 *M* thorium nitrate (1 Q:1 Th), all in methanol, are compared over the range 400–600 mμ. Inasmuch

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[1] Illinois Institute of Technology, Chicago, Illinois.

[2] Frank, Clark and Coker, THIS JOURNAL, **72**, 1827 (1950).

[3] Job, *Ann. chim.*, [10] **9**, 113 (1928).

[4] Vosburgh and Cooper, THIS JOURNAL, **63**, 437 (1941).