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.

(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

BY THERALD MOELLER AND EDWARD H. KOBISK[1]

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.

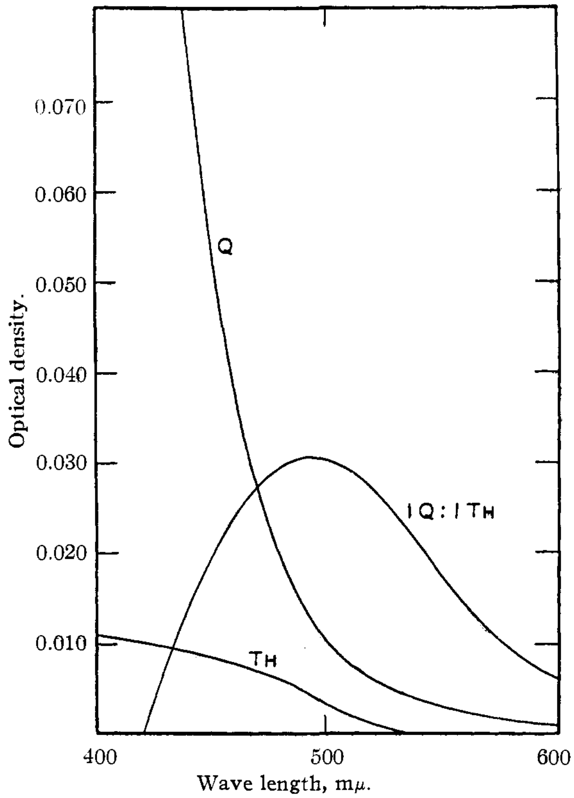

Fig. 1.—Absorption spectra of 2,5-dihydroxyquinone (Q), thorium nitrate (Th), and an equimolar mixture of the two (1 Q:1 Th) in methanol.

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).

as spectra for solutions containing other mole ratios of the quinone to thorium were exactly similar to that given for the 1:1 combination, they are not included. Since all such solutions showed maximum absorption at 490 mμ, but a single absorbing species is present in them. The optical density difference–composition curve[4] given in Fig. 2 for data obtained at 490 mμ indicates the presence of two 2,5-dihydroxyquinone groups to one thorium in the colored substance. Decision as to whether this species is a neutral molecule, in which both of the acidic hydrogens in each of the quinone molecules have been replaced by thorium, or an ionic material, in which only a single hydrogen in each of the quinone groups has been involved, cannot be made from data presented here. In any event, a chelate structure seems likely.

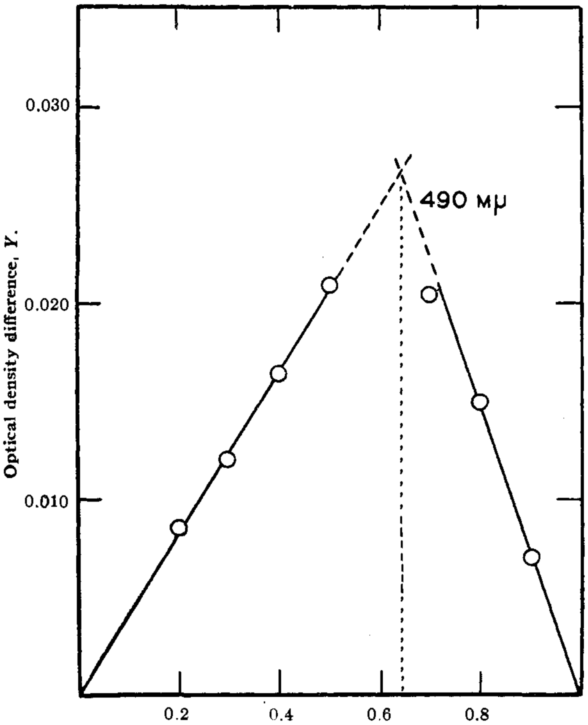

Fig. 2.—Variation of optical density difference (Y) with mole fraction (x) of 2,5-dihydroxyquinone.

Experimental

Materials Used.—Methanol solutions of thorium nitrate were prepared from the pure tetrahydrate and standardized by evaporating, igniting to the oxide and weighing. The 2,5-dihydroxyquinone was prepared by Mr. J. M. Coker[2] and purified by sublimation at 185°. Standard solutions in methanol were prepared by direct weighing.

Spectrophotometric Measurements.—All absorption spectra were obtained with a General Electric Recording Spectrophotometer, using 1-cm. cells and a 10 mμ slit width. In applying the method of continuous variations, the absorption spectra of a series of solutions, prepared by combining varying volumes of 0.001 *M* thorium nitrate and 2,5-dihydroxyquinone solutions, were measured, all solutions having the same total volume. For each the difference between the measured optical density (at the selected wave length) and that calculated for the reagents present assuming no interaction was related to solution composition as in Fig. 2. The maximum at mole fraction 0.64 for the quinone agrees well with the value of 0.67 required by a 2:1 composition for the colored complex. Data at other wave lengths yield the same result.

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Studies in the Guanidine Series. I. The Reaction of Hydrazine with Carbon Tetrachloride and Carbon Tetrabromide

By Seymour H. Patinkin and Eugene Lieber

Triaminoguanidine hydrochloride, $(H_2NNH)_2C(=NNH)\cdot HCl$, was first reported to have been prepared by Stollé[1] by the action of hydrazine hydrate on carbon tetrachloride at its boiling point in the presence of ammonia gas. No details as to actual quantities of materials used or yield obtained were stated. Stollé[1] indicated that further investigations were being carried out; however, nothing has appeared in the literature on this reaction since that time.

A repetition of this work by the writers has failed to confirm this, hydrazine monohydrochloride being identified as the only solid product of the reaction. The results of a number of runs of the reaction of hydrazine with carbon tetrachloride, at its boiling point at atmospheric pressure, either in the presence or absence of a stream of ammonia gas, are summarized in Table I. Slightly increasing the ammonia pressure above atmospheric increases the yield of solids salts in which only ammonium chloride and hydrazine monohydrochloride can be identified. An inert gas, identified as nitrogen, is continuously evolved from the reaction and an examination of the liquid volatile products by infrared analysis showed the presence of chloroform and possibly methylene dichloride. These data are sum-

TABLE I

THE REACTION OF HYDRAZINE WITH CARBON TETRACHLORIDE[a] AT ITS BOILING POINT

				Product			
Run	Hydrazine, g.	Reflux, hr.	Stream of NH_3 gas	Yield,[b] g.	M. p.,[c] °C.	Assay,[d] % N_2H_4	Benzaldehyde derivative, m. p., °C.
1	3.8[e]	48	None	3.2	89	46.73	92.5[f]
2	23.6[g]	18	Yes	4.9	89	46.67	92.5
3	20.4[h]	16	Yes	1.6	87	46.70	90.5
4	20.7[g]	20	None	0.3	88.7	46.50	92
5	18.2[g]	35	Yes	3.1	89	...	92

[a] Excess of CCl_4 used in all runs. [b] Of recrystallized product. [c] All melting points are taken on the Dennis Bar (L. M. Dennis and R. S. Shelton, THIS JOURNAL, **52**, 3129 (1930)); the m. p. of $N_2H_4\cdot HCl$ is reported to be 89° by Curtius and Jay, *J. prakt. Chem.*, [2] **39**, 27 (1889), [d] The theoretical hydrazine content of $N_2H_4\cdot HCl$ is 46.72%. [e] Anhydrous N_2H_4. [f] Benzalazine $(C_6H_5CH:N)_2$ is reported to melt at 93° (Beilstein, Vol. VII, p. 225). [g] 85% hydrazine hydrate. [h] 95% hydrazine hydrate.

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[1] R. Stollé, *Ber.*, **37**, 3548 (1904).