

The Reaction of Thorium Nitrate Tetrahydrate with Nitrogen Oxides. Anhydrous Thorium Nitrate¹

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The preparation of certain anhydrous nitrates is very difficult. Guntz and Martin⁴ have reported the preparation of the anhydrous nitrates of Mn(II), Cu(II), Ni(II) and Co(II) by the condensation of dinitrogen pentoxide on a nitric acid solution of the hydrate. Markétos⁵ and Späth⁶ prepared anhydrous uranyl nitrate by dehydration of the hydrate in an atmosphere of nitrogen oxide vapors. Jander⁷ prepared anhydrous nitrates by the reaction of anhydrous nitric acid with metallic picrates. The reaction of metallic oxides with liquid dinitrogen tetroxide has also produced anhydrous nitrates.⁸⁻¹⁰ Recently this reaction has been more extensively investigated by Addison,^{11,12} Gibson and Katz¹³ and Ferraro and Gibson.¹⁴

Kolb¹⁵ first reported the preparation of an anhydrous thorium nitrate. Misciatelli¹⁶ also reported the preparation of an anhydrous thorium nitrate by condensation of dinitrogen pentoxide on a nitric acid solution of the hydrate.

The present paper deals with several procedures investigated for the preparation of anhydrous thorium nitrate. Of these only the reaction of thorium nitrate tetrahydrate with dinitrogen pentoxide in anhydrous nitric acid to form $\text{Th}(\text{NO}_3)_4 \cdot 2\text{N}_2\text{O}_5$ was completely successful. The thermal decomposition of $\text{Th}(\text{NO}_3)_4 \cdot 2\text{N}_2\text{O}_5$ yielded anhydrous thorium nitrate.

Experimental

Materials: (a) $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$, prepared as described in an earlier publication¹⁷; (b) 100% HNO_3 , General Chemical Division Grade (total acidity 100% min.); (c) thorium metal, obtained from the Special Materials Division, Argonne National Laboratory; (d) ThO_2 , prepared by the thermal decomposition of C.P. $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ at 550°; (e) N_2O_4 , Matheson Cylinder, dried before use by passing through a tower containing P_2O_5 ; (f) N_2O_5 , produced by dropping anhydrous nitric acid on solid phosphorus pentoxide.

Analyses.—Nitrogen dioxide in the solids was determined by ceric sulfate titration.¹⁸ Thorium nitrate was deter-

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(4) A. Guntz and F. Martin, *Bull. soc. chim. France*, [4] **5**, 1004 (1909).

(5) M. Markétos, *Compt. rend.*, **155**, 210 (1912).

(6) E. Späth, *Monatsh.*, **33**, 853 (1912).

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(14) J. R. Ferraro and G. Gibson, *ibid.*, **75**, 574 (1953).

(15) A. Kolb, *Z. anorg. Chem.*, **83**, 143 (1913).

(16) P. Misciatelli, *Gazz. chim. ital.*, **60**, 882 (1930).

(17) J. R. Ferraro, L. I. Katzin and G. Gibson, *THIS JOURNAL*, **76**, 1909 (1954).

(18) G. Frederick Smith, "Ceric Sulfate," Vol. I, G. F. Smith Chem. Co., Columbus, Ohio, 1935.

mined by ignition of the sample to thoria (ThO_2). Water was determined by titration with the Karl Fischer reagent.¹⁹ Nitrogen analyses were made using the du Pont nitrometer method.²⁰

Apparatus and Procedure. (a) **Reaction of Thorium Nitrate Tetrahydrate with Dinitrogen Pentoxide in Anhydrous Nitric Acid at 25°.**—A conventional vacuum line was used in carrying out the reactions. The reaction flask could be removed from the remainder of the system without exposing the contents to the atmosphere. A weighed amount of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (1–2.5 g.) was added to a known volume (10–20 ml.) of anhydrous nitric acid in the reaction flask and dinitrogen pentoxide condensed onto the mixture. The dinitrogen pentoxide was carried into the flask from the N_2O_5 generator by means of a current of dry oxygen. After sufficient dinitrogen pentoxide had been condensed the mixture was distilled to remove the anhydrous nitric acid. The stopcocks of the reaction flask were then closed and the flask was transferred to a dry-box for sampling.

(b) **Reaction of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ with N_2O_5 at 140–180°.**—Gaseous dinitrogen pentoxide was passed into a tube containing $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ on a fritted filter disc. An electric sleeve furnace was fitted around the reaction tube for the purpose of maintaining a fixed temperature for the different experiments (the range of temperatures investigated was varied from 140–180°). A typical sample had the following analyses: Th, 49.94; H_2O , 5.83; NO_2 , 1.41. Assuming that the remainder is nitrate it can be calculated that the NO_3^-/Th ratio is 3 and that some decomposition of the nitrate had occurred.

(c) **Reaction of Metallic Thorium and Thorium Oxide with Liquid Dinitrogen Tetroxide.**—The apparatus and experimental procedure for this type of reaction have been described elsewhere.¹³ The metallic thorium consisted of filings, while the oxide was prepared from the oxalate at 550°. There appeared to be no evidence for a reaction even after heating the reaction tubes at 87° and 14.5 atm. in a pressure bomb for 7 hours.

Discussion

Reaction of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ with N_2O_5 in Anhydrous HNO_3 at 25° (Table I).—With an increase in the $\text{N}_2\text{O}_5/\text{hydrate}$ ratio the solids obtained showed a decrease in water and nitrogen dioxide content and an increase in dinitrogen pentoxide. When a large mole excess (5.5 times or greater) of

TABLE I
REACTION OF $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ WITH N_2O_5 IN ANHYDROUS HNO_3 AT 25°

Run	G. N_2O_5 G. tetra- hydrate	Added mole excess of N_2O_5^a	Analyses of products of reaction, %			
			ThO_2	NO_2	H_2O	N_2O_5 (by diff.)
1	6.4	8.2	37.99	Nil ^b	Nil ^b	30.94 ^c
2	6.3	8.1	37.96	Nil	Nil	31.00
3	6.3	8.1	37.80	Nil	Nil	31.29
4	5.2	6.7	36.85	0.36	Nil	32.65
5	4.3	5.5	37.71	0.10	Nil	31.45
6	3.9	5.0	39.35	3.75	Nil	24.72
7	3.2	4.2	38.48	3.42	0.41	26.22
8	2.1	2.7	40.91	4.67	0.72	20.14
9	1.6	2.0	40.08	10.29	5.41	11.47
Theoretical for $\text{Th}(\text{NO}_3)_4 \cdot 2\text{N}_2\text{O}_5$			37.94	31.03

^a Mole excess of N_2O_5 defined as added moles of N_2O_5 /theoretical moles of N_2O_5 necessary to react with the water in $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$. ^b Nil is defined as less than 0.1%. ^c Solid contained 16.13% total nitrogen by the du Pont nitrometer method. (Theory for total nitrogen in $\text{Th}(\text{NO}_3)_4 \cdot 2\text{N}_2\text{O}_5$, 16.01%.)

(19) J. Mitchell, Jr., and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948.

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dinitrogen pentoxide was added the product obtained corresponded to a composition $\text{Th}(\text{NO}_3)_4 \cdot 2\text{N}_2\text{O}_5$. With the addition of smaller amounts of dinitrogen pentoxide, solids with as much as 3 moles of NO_2 per mole of $\text{Th}(\text{NO}_3)_4$ have been obtained. The anhydrous nitric acid may be one possible source of the nitrogen dioxide found in these solids, since the NO_2 content of the acid may run as high as 5%. These nitrogen dioxide solids contain varying amounts of water and may contain as much as 1 mole of water per thorium nitrate.

The dinitrogen pentoxide addition compound is a white, granular solid which dissolved in water with the evolution of heat. The nitrogen dioxide containing solids are creamy white and flaky and dissolved in water with the liberation of nitrogen dioxide. When desiccated over 98% sulfuric acid for one week the dinitrogen pentoxide addition compound remained comparatively stable while the corresponding nitrogen dioxide solids lost weight. This weight loss was due in part to an evolution of nitrogen dioxide.

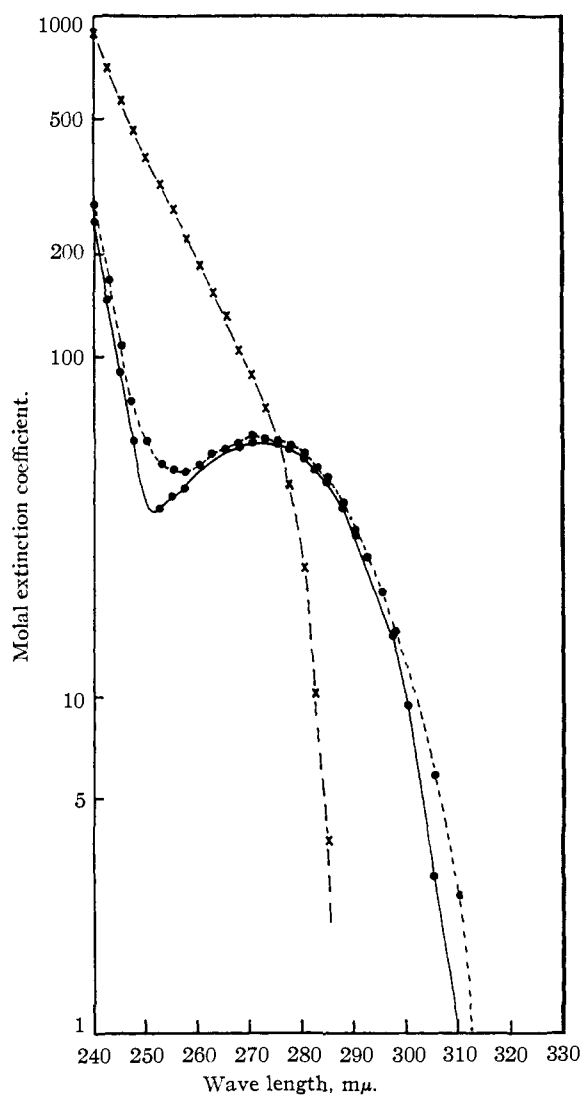


Fig. 1.—Absorption spectra in diethyl ether at 25°C: —x—, $\text{Th}(\text{NO}_3)_4$; —, $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$; —, $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$.

The powder X-ray diffraction patterns of the dinitrogen pentoxide solids, nitrogen dioxide solids and anhydrous thorium nitrate are different from one another and are also different from the powder X-ray diffraction patterns of the hydrates of thorium nitrate and of thorium oxide (ThO_2).

All of the dinitrogen pentoxide and nitrogen dioxide coordinated solids were diamagnetic. This is the expected result with the dinitrogen pentoxide solids. With the nitrogen dioxide solids the results are in agreement with those of Sisler and co-workers,²¹ who found that the addition compounds of dinitrogen tetroxide and ethers were also diamagnetic, indicating that the ligand is probably present as the diamagnetic N_2O_4 rather than the paramagnetic NO_2 .

Thermal Decomposition of $\text{Th}(\text{NO}_3)_4 \cdot 2\text{N}_2\text{O}_5$. Preparation of Anhydrous $\text{Th}(\text{NO}_3)_4$.—Following the procedure used by Ferraro and Gibson¹⁴ 1 to 2 gram samples of $\text{Th}(\text{NO}_3)_4 \cdot 2\text{N}_2\text{O}_5$ were heated at 150–160° at 10^{-5} mm. pressure for 4 to 5 hours. The solid obtained was white and powdery. A typical sample had the following analysis: Calcd. for $\text{Th}(\text{NO}_3)_4$: ThO_2 , 55.01; N, 11.67. Found: ThO_2 , 54.80; N, 11.88; H_2O , nil; NO_2 , nil. The nitrogen analyses correspond to a 0.4% excess of dinitrogen pentoxide. Thermal decomposition of the dinitrogen pentoxide solids gave solids which consistently analyzed for thoria close to the composition of anhydrous thorium nitrate. It was apparent, however, that it was increasingly difficult to remove the last traces of dinitrogen pentoxide. For example, thermal decomposition at 10 mm. pressures and 150–160° for 5 hours gave solids with 53–54% thoria. It was then necessary to raise the temperature to 170–175°, and maintain this temperature for about 2 hours, in order to remove most of the remaining dinitrogen pentoxide and approach the composition of the anhydrous solid. Thermal decomposition of the dinitrogen tetroxide solids (contain 3% or more of water) is accomplished more readily, but there appears to be a concurrent decomposition of the nitrate in addition to removal of the coordinated dinitrogen tetroxide. The presence of water in these compositions undoubtedly contributes to the decomposition through a hydrolysis mechanism.

The anhydrous salt dissolved readily in water giving a clear solution, spectrophotometrically identical with solutions of thorium nitrate tetrahydrate and pentahydrate. In anhydrous diethyl ether dissolution is difficult. The absorption spectrum of such a solution is compared with the spectrum of ether solutions of the tetrahydrate and the pentahydrate in Fig. 1, and shows marked differences.

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Anion-exchange Studies. XII.^{1,2} Adsorption of Acids by Strong Base Anion-exchange Resins in Polyvalent Forms. Separation of Weak and Strong Acids

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In previous communications,^{3,4} it was demonstrated that a strong base anion-exchange resin in the sulfate form can adsorb strong acids and that this property can be utilized to separate strong acids from salts. In these earlier communications it was implied that this adsorption of acids should not be restricted to the sulfate form of the resin but should also occur with resins containing other polyvalent ions, *e.g.*, phosphates, citrates, etc. Additional experiments have now been carried out which confirm this hypothesis.

Since adsorption of strong acids by the polyvalent forms of anion-exchange resins probably involves an acid-base reaction, it appeared probable that weak acids such as acetic acid, boric acid, as well as non-electrolytes, should show considerably less absorption and hence should be separable from strong acids. However, ion-exchange resins appear to have unusual solvent properties for some organic materials such as indicated, for example, by the widely varying selectivities of ion exchange resins for various organic acids.⁵ Hence, successful separation of weak acids and non-electrolytes from strong acids probably depends on absence of significant acid-base reactions as well as on absence of unusual solvent properties of the resin.

1. Adsorption of Acids by Polyvalent Forms of Strong Base Anion-exchange Resins.—As an extension of the work on the adsorption of sulfuric acid by the sulfate form of a strong base anion-exchange resin, the adsorption of phosphoric acid by the phosphate form of the resin was investigated, as well as adsorption of hydrochloric acid and citric acid by the citrate form of the resin. The resin (200–230 mesh) was from the same batch of the quaternary amine polystyrene divinylbenzene resin (Dowex-1) used in the earlier work.^{3,6} Adsorption was demonstrated by a column method. Acids were passed into *ca.* 7.5-ml. columns of cross-sectional area 0.5 cm.² at a flow rate of *ca.* 0.5 cm./min. and the break-through volume determined by acid-base titrations of the effluent. The phosphate and citrate forms of the resin⁷

were prepared in a manner analogous to the method used for the preparation of the sulfate forms,⁴ *i.e.*, by passing concentrated solutions of ammonium citrate (*pH* 8) or sodium phosphate (*pH* 11) through the chloride form of the resin until there was a negative chloride test in the effluent and then washing the resin extensively with water.

The results of some typical experiments are illustrated in Fig. 1, which is divided into four parts. Part A illustrates the adsorption of 0.08 *M* H₂SO₄ by the sulfate form of the resin, part B, the adsorption of 0.25 *M* H₃PO₄ by the phosphate form, part C, the adsorption of 0.24 *M* citric acid by the citrate form, and part D, the adsorption of 0.5 *M* HCl by the citrate form. The apparent interstitial volume of the columns was taken to be 42%⁸ of the total column volume and is shown by a dashed line in the figures. As seen from Fig. 1, several column volumes of the acids can be passed through the columns before significant break-through of acid occurs and thus it appears that adsorption of acids by the polyvalent forms of the anion exchangers is general. In addition, as shown in part C, for the citrate form of the resin regeneration by water elution is at least partially successful, as it also was for the sulfate form, since *ca.* 60% of the adsorbed citric acid was removed in four volumes of water wash.

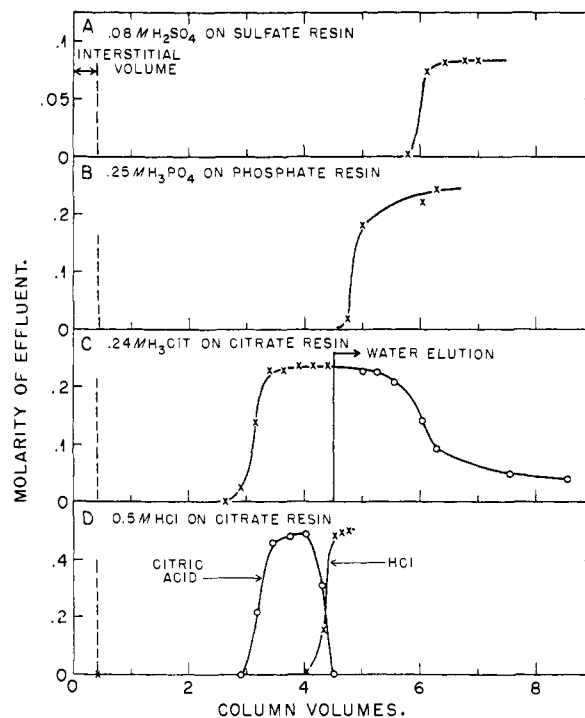


Fig. 1.—Adsorption of acids by polyvalent forms of anion-exchange resins.

In experiment D, acid-base titrations were supplemented by chloride titrations (AgNO₃). The results show that hydrochloric acid can be adsorbed by the citrate form of the resin and that on extensive treatment with hydrochloric acid, citric acid is essentially completely removed before

(1) This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

(2) Previous paper, K. A. Kraus and F. Nelson, *THIS JOURNAL*, **76**, 5916 (1954).

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(4) K. A. Kraus and F. Nelson, *ibid.*, **75**, 3273 (1953).

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