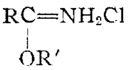
Imidoester Hydrochlorides

BY C. A. MACKENZIE, G. A. SCHMIDT AND L. R. WEBB[1]

A number of imidoester hydrochlorides were made by the Pinner reaction. These compounds are listed in Table I.

TABLE I

IMIDOESTER HYDROCHLORIDES 

$$\underset{\displaystyle OR'}{RC}{=}NH_2Cl$$

R	R'	Dec. pts., °C.	Chlorine, % Calcd.	Chlorine, % Found
$ClCH_2CH_2-$	$C_6H_5CH_2-$	79–81	15.2	15.1
$ClCH_2CH_2-$	$m\text{-}NO_2C_6H_4CH_2-$	89–90	12.7	12.7
$ClCH_2CH_2-$	$p\text{-}NO_2C_6H_4CH_2-$	89–90	12.7	12.7
$ClCH_2CH_2-$	C_6H_5-	130–131	16.6	16.6
C_6H_5-	$C_6H_5CH_2-$	90–91	14.3	14.3
C_6H_5-	$m\text{-}NO_2C_6H_4CH_2-$	105–106	12.1	12.1
C_6H_5-	$p\text{-}NO_2C_6H_4CH_2-$	122–123	12.1	12.1
C_6H_5-	C_2H_5-	128–129	19.6	19.6
CH_3-	$C_6H_5CH_2-$	102–103	19.1	19.1
CH_3-	$m\text{-}NO_2C_6H_4CH_2-$	115–116	15.8	15.8
CH_3-	$p\text{-}NO_2C_6H_4CH_2-$	114–116	15.8	15.8
			Nitrogen, %	
$ClCH_2CH_2-$	$n\text{-}C_4H_9-$	102–103	7.0	6.9
$ClCH_2CH_2-$	$n\text{-}C_7H_{15}-$	103–105	5.8	5.7

The reactions were carried out both in the presence of ether and in its absence. Better yields were obtained when ether was not used; however, in such cases, longer periods of time were required for complete crystallization to occur. With either method the yields of product exceeded 75%. The nitriles and alcohols (and ether) were used in equimolar quantities and were saturated with dry hydrogen chloride, then placed in stoppered flasks in a refrigerator until crystallization was complete. Crystallization was complete, usually within a 24-hour period although benzyl imidobenzoate hydrochloride, in the absence of ether, required seven days.

It was not found possible to recrystallize the salts without considerable decomposition occurring; for this reason these compounds should be prepared only from carefully purified reagents. They may be stored indefinitely in a refrigerator; if they are left in a desiccator at room temperature they may decompose. When benzyl β-chloroimidopropionate hydrochloride was stored at room temperature it completely decomposed in about four days to benzyl chloride and β-chloropropionamide.

n-Heptyl β-chloropropionate was obtained as the hydrolysis product of *n*-heptyl β-chloroimidopropionate hydrochloride. *Anal.* Calcd. for $C_{10}H_{19}O_2Cl$: Cl, 17.2. Found: Cl, 17.2; b.p. 86° (2 mm.); d^{25} 0.9715; $n^{25}\text{D}$ 1.4360.

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On the Structure of Nitrogen Hydrogen Sulfide

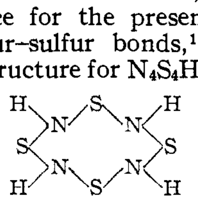
BY ELLIS R. LIPPINCOTT AND MARVIN C. TOBIN

In the course of a spectroscopic study of nitrogen tetrasulfide, we had occasion to prepare a sample of nitrogen hydrogen sulfide, $N_4S_4H_4$, and examine its infrared spectrum in the region 280–3700 cm.$^{-1}$. The spectra were taken of a Nujol mull of the powder. The regions from 670–1700, and from 1700–3700 cm.$^{-1}$ were covered on a Beckmann IR-2 spectrometer at the Spectroscopy Laboratory of the University of Connecticut, using rock salt and lithium fluoride prisms. The region 280–670 cm.$^{-1}$ was covered on a Perkin–Elmer spectrometer, at the Spectroscopy Laboratory of the Massachusetts Institute of Technology, using potassium bromide and thallium bromide–iodide prisms. The absorption peaks in cm.$^{-1}$ observed in the above regions are 293(m), 407(s), 462(s), 516(m), 541(m), 693(w), 712(w), 828(s), 1262(m), 1296(m), 1302(m), 3220(s), 3285(s) and 3320(m), respectively.

The sample was prepared by the method of Meuwesen,[1] by reduction of nitrogen tetrasulfide, N_4S_4, in benzene with alcoholic $SnCl_2$.

It is believed that $N_4S_4H_4$ has a cyclic structure, based on the fact that it is prepared by reduction from cyclic[2] N_4S_4. However, while most observers believe,[1,3] on the basis of chemical evidence, that the hydrogens are bound to the sulfur atoms, in $N_4S_4H_4$, the presence of strong bands at 3220, 3285 and 3320 cm.$^{-1}$, and the absence of any bands in the region 2600 cm.$^{-1}$ in the infrared spectrum, indicates the presence of NH rather than of SH bonds in the molecule.

On the basis of the above data, and the lack of chemical evidence for the presence of nitrogen–nitrogen or sulfur–sulfur bonds,[1,3,4] we feel that the most likely structure for $N_4S_4H_4$ is



and that the compound should be called cyclotetrathiotetraimine.

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[1] A. Meuwesen, *Ber.*, **62**, 1959 (1929).

[2] C. S. Lu and J. Donahue, THIS JOURNAL, **66**, 818 (1944).

[3] Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, New York, N. Y., Vol. II, 1950, p. 893.

[4] A. Meuwesen and H. Holch, *Ber.*, **64B**, 2301 (1931).

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The Thorium Nitrate–Water System Above 20°

BY W. L. MARSHALL, J. S. GILL AND C. H. SECOY

Misciatelli[1] has determined the ice curve and the solubility of a hexahydrate of thorium nitrate from the cryohydric temperature up to 20°. We have extended these data to 211° to show a transition from the hexahydrate to a tetrahydrate at 111° and a transition of the tetrahydrate to a lower hydrate at approximately 151°.

The data are given in Tables I and II and in Fig. 1. These results are in good agreement with Misciatelli's solubility curve below 20° and serve to verify his determination of the hexahydrate as the stable solid phase at 20°.

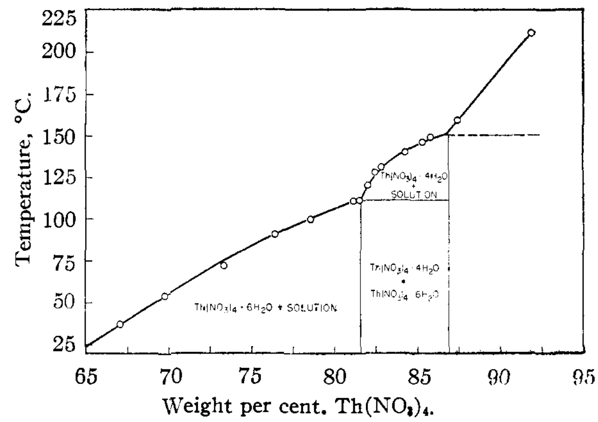

Fig. 1.—The thorium nitrate–water system above 20°.

Decomposition of the system was indicated above approximately 115° by the slight odor of nitric acid and also by the partial vapor coloration above approximately 140°. However, the rate of decomposition appeared sufficiently slow so as not to invalidate data obtained above these temperatures.

TABLE I

THE SOLUBILITY OF THORIUM NITRATE IN WATER, 37–211°

Method of determination	Temp., °C.	Liquid, per cent. $Th(NO_3)_4$	Solid, per cent. $Th(NO_3)_4$	Solid phase
Analytical	37.3	67.07	81.18 (theor., 81.62)	$Th(NO_3)_4 \cdot 6H_2O$
Analytical	54.5	69.78		$Th(NO_3)_4 \cdot 6H_2O$
Analytical	72.0	73.39		$Th(NO_3)_4 \cdot 6H_2O$
Analytical	90.2	76.39	80.82 (theor., 81.62)	$Th(NO_3)_4 \cdot 6H_2O$
Analytical	99.7	78.56		$Th(NO_3)_4 \cdot 6H_2O$
Analytical	110.4	81.11		$Th(NO_3)_4 \cdot 6H_2O$
Analytical	110.9	81.50		$Th(NO_3)_4 \cdot 6H_2O$
	111[a]			$Th(NO_3)_4 \cdot 6H_2O + Th(NO_3)_4 \cdot 4H_2O$
Analytical	120.6	82.01		$Th(NO_3)_4 \cdot 4H_2O$
Synthetic	128	82.41		$Th(NO_3)_4 \cdot 4H_2O$
	129.5		85.84 (theor., 86.95)	$Th(NO_3)_4 \cdot 4H_2O$
Analytical	130.5	82.85		$Th(NO_3)_4 \cdot 4H_2O$
Analytical	139.5	84.27		$Th(NO_3)_4 \cdot 4H_2O$
Analytical	146.0	85.30		$Th(NO_3)_4 \cdot 4H_2O$
Analytical	149.0	85.81		$Th(NO_3)_4 \cdot 4H_2O$
	151[b]			$Th(NO_3)_4 \cdot 4H_2O + Th(NO_3)_4 \cdot XH_2O$
Synthetic	159	87.41		$Th(NO_3)_4 \cdot XH_2O$
Synthetic	211	91.82		$Th(NO_3)_4 \cdot XH_2O$

[a] Intersection temperature for melting point of the hexahydrate. [b] Intersection temperature for melting point of the tetrahydrate.

TABLE II

MELTING POINT DETERMINATIONS

Weight per cent. $Th(NO_3)_4$	82.41	83.72	91.82
First observed melting (T, °C.)	105–115	105–115	~160

Transition temperatures of the hexahydrate and tetrahydrate were determined from intersection points of the graphic data, from a series of cooling curves, and from initial melting points of solid mixtures in the appropriate concentration ranges. From the cooling curves the best temperature for the hexahydrate to tetrahydrate transition was fixed at 111.3 ± 0.4° after three recrystallizations. Melting point data given in Table II were rather difficult to obtain due to the small concentration differences between successive hydrates.

Experimental

Chemically pure thorium nitrate tetrahydrate obtained from the Maywood Company was used. Solubility data from 37 to 150° were obtained analytically by stirring thorium nitrate solutions in the presence of excess solid for about 40 minutes in a 200-cc. round-bottom flask set in a thermostat controllable to ±0.05°. The approach to equilibrium was made from both directions on the temperature scale to verify true equilibration. Preliminary sampling had shown that stirring for 10 to 15 minutes was a sufficient time for the establishment of equilibrium. The stirrer was stopped, the solid was allowed to settle, and duplicate samples of the clear solution were taken. These samples were weighed, evaporated to dryness and ignited directly to ThO_2 at 900°. The maximum deviation of duplicates was approximately ±0.15%.

Solubility data above 125° accurate to ±1° were obtained in 4 and 6 mm. i.d. silica tubing by a synthetic method.[2] The solubility temperature of a $Th(NO_3)_4$–H_2O

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[1] P. Misciatelli, *Gazz. chim. ital.*, **60**, 833 (1930).

[2] C. H. Secoy, THIS JOURNAL, **72**, 3343 (1950).