Cr^{++}[11,12] (unless this exchange which takes place by Cr^{++}–$Cr(H_2O)_6^{+++}$ electron transfer is itself catalyzed—and this is entirely possible—it will not significantly affect the results).

Published kinetic data[2] when extrapolated to the temperature of the present experiments show that in the 3rd experiment of Table I approximately 52% of the reaction proceeds by the aquo path. The observation that oxygen transfer is substantially 100% proves that not only by the hydroxo path but also by the aquo path electron transfer is accompanied by oxygen transfer, and a bridged activated complex is indicated for both paths. This conclusion is supported by the other data which extend to higher and lower acidity so that the relative contribution of the two paths to the total reaction is changed.

An earlier experiment[13] in which evidence for a doubly bridged activated complex was sought in the reaction of *cis*-$Co\text{-}en_2Cl_2^+$ with Cr^{++} was inconclusive owing to the rapid dissociation of $CrCl_2^+$ brought about by Cr^{++}. The reactions described in the present paper are free from a similar difficulty. As has been mentioned, the exchange of $Cr(H_2O)_6^{+++}$ with water brought about by Cr^{++} is so slow as not materially to affect our results. We find that even when *cis* Co(III) ions are oxidizing agents, one and only one atom of oxygen is transferred to the reducing agent. The range of acid covered in the experiment is large enough so that this conclusion can probably be taken to apply to the aquo path and to the hydroxo path. However, the dihydroxy path may not be significantly featured even at our lowest acidities and the question of the extent of transfer by this path is left open.

It should be mentioned explicitly that the present results prove that a seven-coördinated aquochromic ion is not formed as an intermediate product in the reactions studied. Such an intermediate would arise for example if the water molecule from the Co(III) complex were presented to the face of the octahedron about the Cr^{++}. If such an intermediate were formed it would lead to loss to solvent of at least $^1/_7$ of the labelled water. The results thus provide some support for the view that the bridging group occupies one of the normal coördination positions about the chromium, but they by no means constitute proof because alternative formulations remain.

The experiments at high Cl^- and Br^- show that these ions do function as non-bridging ligands, although not very efficiently. Whether oxygen transfer takes place by the paths involving the halide ion is not known, and it will in fact be very difficult to find out because the process $CrX^{++} + Cr^{++}$ [14,15] provides for very rapid exchange of water between $(H_2O)_5CrX^{++}$ and solvent. The participation of Cl^- in the reaction of $Co(NH_3)_6^{+++} + Cr^{++}$ has been demonstrated and this reaction does not involve a bridged activated complex. It is thus possible that the reaction of $(NH_3)_5CoH_2O^{++}$ with $CrCl^+$ takes place by an analogous mechanism. The specific rate coefficient for the term $(Co(NH_3)_6^{+++})(Cr^{++})(Cl^-)$ is 0.7 at 25°, $\mu = 0.4$. From the present results, the coefficient for the rate term $(Co(NH_3)_5H_2O^{+++})(Cr^{++})(Cl^-)$ at $\mu = 1.0$ is estimated as 2×10^1. The rate comparison is consistent with the view that the reaction takes place by similar mechanisms, the Cl^- acting to bring the electron from the Cr^{++} to the exterior of the first coördination shell.

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[11] R. A. Plane and H. Taube, *J. Phys. Chem.* **19**, 602 (1951).

[12] A. Anderson and N. A. Bonner, THIS JOURNAL, **76**, 3826 (1954).

[13] H. Taube and H. Myers, *ibid.*, **76**, 2103 (1954).

[14] H. Taube and E. L. King, *ibid.*, **76**, 4053 (1954).

[15] D. L. Ball and E. L. King, *ibid.*, **80**, 1091 (1958).

[16] A. Zwickel, Ph.D. Dissertation, University of Chicago, 1959.

[CONTRIBUTION FROM THE W. A. NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

The Phosphonitrilic Isothiocyanates

BY G. TESI, R. J. A. OTTO, F. G. SHERIF AND L. F. AUDRIETH

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The preparation of the trimeric (I) and tetrameric (II) phosphonitrilic isothiocyanates, $[PN(NCS)_2]_{3,4}$, is best accomplished by reaction between the chlorides and alkali metal (ammonium) thiocyanates in acetone. Derivatives of I and II are obtainable by reaction with compounds containing NH_2, OH and N_2H_3 groups. Both I and II polymerize on heating to rubber-like gels.

Non-metallic inorganic (iso)thiocyanates are usually prepared by allowing the corresponding halides, oxy-halides or thio-halides to react with silver, lead or mercury(II) thiocyanate in some inert organic solvent. Since long refluxing of the components is required due to the fact that the heavy metal thiocyanates are insoluble, extensive decomposition often occurs and yields of the desired (iso)thiocyanates are relatively small. In a communication[1] to the Editor reporting the preparation of the trimeric phosphonitrilic isothiocyanate, $[PN(NCS)_2]_3$, an alternative procedure was disclosed entailing the use of alkali metal thiocyanates. It is necessary, however, to make use of non-aqueous solvents in which the phosphonitrilic chlorides are soluble without reaction, and the alkali (ammonium or substituted ammonium) thiocyanates are also appreciably soluble. Interaction then takes place with the precipitation of the alkali metal (ammonium or substituted ammonium) chloride in accordance with the illustrative equation

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[1] R. J. A. Otto and L. F. Audrieth, THIS JOURNAL, **80**, 5894 (1958).

TABLE I

SOLUBILITIES OF THE PHOSPHONITRILIC ISOTHIOCYANATES (IN G./100 G. SOLVENT AT 0°)

Solvent	$[PN(NCS)_2]_3$	$[PN(NCS)_2]_4$
Water	Insoluble	Insoluble
Acetone	5.14	0.1
Ether	20.9	.7
n-Heptane	5.23	.26
Carbon tetrachloride	v.s.	11.2

TABLE II

DERIVATIVES OF THE PHOSPHONITRILIC ISOTHIOCYANATES

$$[PN(NCS)_2]_{3,4} + 6(8)HX \longrightarrow [PN(NHCSX)_2]_{3,4}$$

		M.p., °C.	Analyses, % Calcd. C	H	N	Found C	H	N
HNH_2	$[NP(NHCSNH_2)_2]_3$[a]	190 dec.	12.3	3.1	35.9	12.0	3.7	35.3
	$[NP(NHCSNH_2)_2]_4$[a]	120 dec.	12.3	3.1	35.9	12.5	3.7	26.0
$HNHC_4H_9$	$[NP(NHCSNHC_4H_9)_2]_3$[a]	155	39.1	7.2	22.8	38.8	6.9	22.3
	$[NP(NHCSNHC_4H_9)_2]_4$[a]	105	39.1	7.2	22.8	39.4	7.1	23.2
$HNHC_6H_5$	$[NP(NHCSNHC_6H_5)_2]_3$[c]	151	48.4	4.1	20.2	48.9	4.2	19.6
	$[NP(NHCSNHC_6H_5)_2]_4$[c]	139	48.4	4.1	20.2	48.2	4.2	20.3
HOC_2H_5	$[NP(NHCSOC_2H_5)_2]_3$[b]	174	28.5	4.8	16.6	28.5	4.9	17.0
	$[NP(NHCSOC_2H_5)_2]_4$[b]	189	28.5	4.8	16.6	28.4	4.7	17.3
$HNHNHC_6H_5$	$[NP(NHCSNHNHC_6H_5)_2]_3$[a]	165 dec.	44.6	4.3	26.0	45.1	4.6	25.8
	$[NP(NHCSNHNHC_6H_5)_2]_4$[a]	153 dec.	44.6	4.3	26.0	44.3	4.9	25.8

[a] By direct interaction of components in ether. [b] Refluxing of I and of II in ethanol for one hour and then cooling to 0° to effect crystallization. [c] Benzene as solvent medium.

$$(PNCl_2)_{3,4} + 6(8)KSCN \longrightarrow [PN(NCS)_2]_{3,4} + 6(8)KCl$$

Ketones, nitriles, tertiary amines, tertiary amides, even acetic acid and liquid sulfur dioxide can be employed as solvents for the reactants. We have found it most convenient to use acetone and to employ the potassium or ammonium thiocyanates for reaction with the phosphonitrilic chlorides.

The preparation of the trimeric (I) and tetrameric (II) phosphonitrilic isothiocyanates is described. The reaction products of these compounds with ammonia, amines, alcohols and hydrazine derivatives have been characterized. I and II undergo polymerization to rubber-like products on heating to temperatures above 150°. By contrast, temperatures above 300° are required to effect the bulk polymerization of the corresponding chlorides and fluorides.

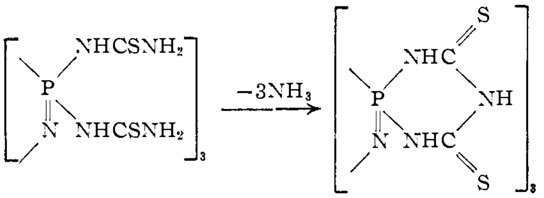
Experimental

Trimeric Phosphonitrilic Isothiocyanate, $P_3N_3(NCS)_6$, (I).—A solution containing 34.77 g. (0.1 mole) of $(PNCl_2)_3$ in 200 ml. of acetone was added to a solution-slurry of 58.3 g. (0.6 mole) of KSCN in 200 ml. of acetone with constant agitation, over a period of ten minutes. The reaction mixture then was heated for a few minutes to the boiling point of acetone, the precipitated KCl removed by filtration and washed thoroughly with warm acetone and the filtrate cooled and kept at the temperature of a Dry Ice bath for at least 2 hr. The white crystalline product was separated by filtration, washed with cold acetone, dissolved in 200 ml. of *n*-heptane and recrystallized by again cooling in a Dry Ice bath. A yield of 41 g. (85%) of the desired compound, m.p. 41–42°, was obtained.[2]

Anal. Calcd. for $P_3N_3(NCS)_6$: C, 14.9; N, 26.1; P, 19.2. Found: C, 15.3; N, 25.8; P, 19.3.

Details concerning molecular weight determinations and structural characterization of the product as an isothiocyanate are given in the original communication.[1] Solubilities in various solvents are given in Table I. Further characterization of I was accomplished by utilizing the highly reactive character of the isothiocyanate groups, bonded to the phosphorus atoms, to prepare adducts by reaction with substances containing one or more reactive NH_2 or OH groups, such as ammonia, *n*-butylamine, aniline, ethanol and phenylhydrazine. Pertinent data are given in Table II. Polyamines and polyhydroxy compounds such as hexamethylenediamine, diethylenetriamine and ethylene glycol also react with I. Semi-quantitative results indicate that reactions of the diamines and of the glycol entail addition of one mole of each per reactive NCS group. Even cellulose reacts in benzene solution to add up to 8% by weight of I.

Treatment of an aqueous solution of the ammonia addition product with concentrated sodium hydroxide, distillation and titration of liberated ammonia indicates that only one-half of the theoretical amount of combined ammonia is eliminated. It is suggested that formation of a dithiobiureto derivative occurs by a deammoniation–cyclization process.



Tetrameric Phosphonitrilic Isothiocyanate, $P_4N_4(NCS)_8$, (II).—A solution containing 46.36 g. (0.1 mole) of $(PNCl_2)_4$ in 400 ml. of acetone was added to a solution-slurry of 77.74 g. (0.8 mole) of KSCN in 200 ml. of acetone with constant agitation, over a period of ten minutes. To ensure completion of the reaction the mixture was warmed to the boiling point of acetone and then cooled to 0°. After standing for several hours the solid product consisting of a *mixture* of potassium chloride and the tetraphosphonitrilic octa-isothiocyanate was separated by filtration, washed with cold acetone and extracted with 400 ml. of hot *n*-heptane. Crystallization was effected by cooling the extract to 0°. Filtration yielded 56 g. (87%) of the desired compound, m.p. 90°.

Anal. Calcd. for $P_4N_4(NCS)_8$: C, 14.9; N, 26.1; P, 19.2. Found: C, 15.2; N, 25.9; P, 19.5.

The solubilities of II in various solvents at 0° are summarized in Table I. II is much less soluble than the trimeric polyhomolog. These differences are reflected in the fact that the preparative procedure for II is much simpler since II precipitates from acetone, the reaction medium.

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[2] Attempts to isolate I by removal of the solvent under reduced pressure led invariably to the formation of a yellow oily product, which on standing frequently would undergo partial solidification. Only limited quantities of I could be recovered by extraction of this residue with *n*-heptane. Even when solutions of I in pure acetone were prepared and subsequently concentrated by evaporation at room temperatures under high vacuum a crystalline product could not be obtained, suggesting some interaction of acetone with the hexaisothiocyanate. To obtain satisfactory yields it is essential (a) to use absolutely anhydrous reagents and solvents, (b) to operate very rapidly in the absence of contact with atmospheric moisture and (c) to carry out filtration and cooling operations quickly. Once the solid material is obtained, recrystallization from *n*-heptane yields a product of high purity.

TABLE III

SOLUBILITY OF POLYMERIZED TRIMERIC PHOSPHONITRILIC ISOTHIOCYANATE IN HOT BENZENE

Temp. of polymn., °C.	Time of polymn., hr.	Wt. dissolved, %
145	1.75	62.2
145	2	21.9
145	6	19.50
145	12	14.96
145	24	14.92
210	10 min.	43.2
210	0.5	21.1
210	1	17.61
210	2	15.65
210	6	14.40
210	12	13.89
210	24	12.08

TABLE IV

SOLUBILITY OF POLYMERIZED TETRAMERIC PHOSPHONITRILIC ISOTHIOCYANATE IN HOT BENZENE

Temp. of polymn., °C.	Time of polymn., hr.	Wt. dissolved, %
180	2	94.0
180	6	16.20
180	12	11.76
180	24	11.71
210	1	45.7
210	2	16.76
210	6	14.49
210	24	9.43

The infrared absorption spectrum verifies the retention of the eight-membered phosphorus–nitrogen ring system and the presence of the isothiocyanate grouping.[1] The molecular weight was determined cryoscopically in benzene. Calcd. for $P_4N_4(NCS)_8$: mol. wt., 644. Found: mol. wt., 601, 606. The presence of reactive isothiocyanate groups was verified, as for I, by formation of adducts with amino, hydroxy and hydrazino compounds, for which pertinent data are given in Table II. Treatment of the octa-thioureido tetraphosphonitrile (ammonia adduct) in aqueous solution also results in the liberation of only one-half of the bound ammonia. Significantly different is the product obtained by reaction with *n*-butylamine. The octa-(N-butylthioureido) tetraphosphonitrile is soluble in ether, the reaction medium. If, however, the ether solution is refluxed a white precipitate, m.p. 155°, gradually separates. The composition and molecular weight of this product correspond to an adduct that can be represented by the empirical formula, $[PN(NCS)_2]_4 \cdot 6C_4H_9NH_2$.

Anal. Calcd. for $[PN(NCS)_2]_4 \cdot 6C_4H_9NH_2$: C, 35.6; H, 6.3; N, 25.2. Found: C, 36.1; H, 6.0; N, 22.9.

Polymerization of the Phosphonitrilic Isothiocyanates.—Heating *in vacuo* or in contact with the atmosphere at higher temperatures results in the gradual conversion of the liquefied isothiocyanates I and II into rubber-like gels. A solubility criterion was adopted to establish the extent of polymerization as a function of time and temperature. The polymerizate was extracted with benzene for 24 hours using glass extraction thimbles containing glass-wool filter pads. Typical results are given in Tables III and IV. For the most highly polymerized samples of both I and II, some 10 to 15% extractable material is still retained in the polymerizate. Up to 210° polymerization was not accompanied by appreciable weight losses; above this temperature the polymerizates became darker in color and more brittle. Weight losses of 27.8 and 16.6% were observed when samples of I were heated for 2 hr. at 300 and 260°, respectively.

Attempts also were made to effect homogeneous polymerization in solvents such as benzene, *n*-heptane, xylene, *o*-dichlorobenzene and nitrobenzene. No solid products were obtained with concentrations of I and of II as high as 20% and with temperatures at the boiling points of the solvents for reflux periods of 48 hr.

Preliminary X-ray diffraction studies of the polymeric phosphonitrilic isothiocyanates under various conditions of temperature and also under tension revealed that the transmission patterns of all samples are similar, consisting of two distinguishable halos corresponding to spacings of 3.5 and 9.5 Å. The possibly analogous phosphonitrilic chloride polymer gives three distinguishable halos (3.35, 6.15, 13.5 Å). These differences suggest a lesser initial order in the case of the polyphosphonitrilic isothiocyanate. X-Ray diffraction patterns of stretched fragments of the most extensible samples (maximum elongation, 200%) failed to show evidences for fiber patterns. If the structure of the polyphosphonitrilic isothiocyanate is imagined to be similar to that of the chloride polymer (*i.e.*, analogous repeating units, chain length and linearity), it is noteworthy that an approximate 400% elongation was required for crystallization in the case of the latter.[3]

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[3] K. H. Meyer, W. Lotmar and G. W. Pankow, *Helv. Chim. Acta*, **19**, 930 (1936).

URBANA, ILLINOIS

The Synthesis of Tetraethyllead by Reaction of Tetravalent Lead Salts with Triethylaluminum and Other Ethyl Metal Compounds[1]

BY FREDERICK W. FREY, JR., AND SHIRL E. COOK

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Lead metal was a by-product of reactions of a number of tetravalent lead salts with alkylmetal compounds. The corresponding reaction with phenylmetal compounds produced no lead metal. A reaction sequence, based on the instability of monoalkyllead salts, is proposed to explain the formation of lead metal as well as the range of organolead yields realized.

The reaction of lead dichloride with ethyl Grignard or ethyllithium represents the conventional laboratory method for the synthesis of tetraethyllead. The reaction of divalent lead salts, in general, with active ethylmetal compounds has been investigated thoroughly.[2] The reactions pro-

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[1] Presented at the 134th meeting of the American Chemical Society, Chicago, Ill., September 11, 1958.

[2] R. W. Leeper, L. Summers and H. Gilman, *Chem. Revs.*, **54**, 108 (1954).