[Contribution from the Armstrong Cork Company, Research and Development Center]

The Reaction of Neutral Esters of Trivalent Phosphorus Acids with Inorganic Acid Chlorides. II. The Reaction of Triphenyl Phosphite with Acid Chlorides of Sulfur Acids

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Triphenyl phosphite reacts readily with sulfuryl chloride, thionyl chloride, sulfur monochloride and sulfur dichloride. With equimolar amounts of sulfuryl or thionyl chloride oxygen abstraction occurs easily at less than 10° under an atmosphere of nitrogen in diffuse light, and even in the dark, to give thionyl chloride or indications of sulfur dichloride, respectively, while triphenyl phosphite is converted to triphenyl phosphate. Sulfuryl chloride is more reactive than thionyl chloride which, in turn, seems to be less reactive than sulfur dichloride. Both sulfur dichloride and sulfur monochloride react rapidly with triphenyl phosphite to give triphenyl phosphorothionate and "triphenoxyphosphorus dichloride." Intermediate addition products could not be isolated or detected. These reactions are considered general for triaryl phosphites, phosphines and other trivalent phosphorus compounds which have no cleavable alkoxy groups.

During studies on phosphorogenic pneumatogens, *i.e.*, phosphorus compounds which decompose into one or more gaseous products, we investigated the reaction of sulfuryl and thionyl chloride with various phosphites. The failure to obtain addition products of sulfuryl chloride with trialkyl phosphites[1] led to an examination of its reaction with triaryl phosphites. Although adducts with inorganic acid chlorides have not yet been reported, it is well known that, in contrast to phosphites bearing an alkyl group, triaryl phosphites give moderately stable addition products with halogens[2,3] and alkyl halides.[2,4] In the present investigation intermediate addition products of triphenyl phosphite with sulfuryl chloride, thionyl chloride, sulfur monochloride or sulfur dichloride were not isolated nor observed. The reactions proceeded rapidly at <10° and apparently even in the absence of light to give products shown in the transformations

$$(PhO)_3P + SO_2Cl_2 \longrightarrow (PhO)_3PO + SOCl_2 \qquad (1)$$

$$(PhO)_3P + SOCl_2 \longrightarrow (PhO)_3PO + SCl_2 \qquad (2)$$

$$2(PhO)_3P + SCl_2 \longrightarrow (PhO)_3PS + (PhO)_3PCl_2 \qquad (3)$$

$$3(PhO)_3P + S_2Cl_2 \longrightarrow 2(PhO)_3PS + (PhO)_3PCl_2 \qquad (4)$$

Sulfur mono- and di-chloride yielded at least 85% of the expected products. We believe these reactions are stoichiometric and the modest recoveries are attributed to difficulties in handling hygroscopic hydrolyzable materials. The reaction with sulfur monochloride provides an interesting experimental confirmation for Morrison's conclusion[5] regarding the reaction of triethyl phosphite with sulfur monochloride. Furthermore, our results with sulfur dichloride cast considerable light on the type of compounds which the Arbuzovs and their co-workers[6] must have obtained but were unable to isolate or identify.[7] The use of triaryl phosphites in gaining a better understanding of the Michaelis–Arbuzov and related reactions of acid chlorides[5,6,8-10] is clearly demonstrated by our studies.

The ease with which these reactions proceed in non-polar solvents such as petroleum ether and the failure to find any evidence for quasi-phosphonium intermediates even at low temperatures suggests a radical mechanism.[11] If one accepts an expanded valence shell for phosphorus[12] the course of reaction involving sulfur dichloride is interpreted readily in terms of a free radical mechanism similar to that proposed by Walling and Rabinowitz[13] for reactions involving dialkyl disulfides and trialkyl phosphites.

$$(ArO)_3P + SCl_2 \longrightarrow [(ArO)_3\overset{..}{P}—\bar{S}Cl_2] \longrightarrow (ArO)_3\dot{P}—Cl + Cl—S\cdot \qquad (5)$$

$$ClS\cdot + (ArO)_3P \rightleftarrows (ArO)_3\dot{P}—S—Cl \qquad (6)$$

$$(ArO)_3\dot{P}—S—Cl + (ArO)_3P \longrightarrow (ArO)_3P{=}S + (ArO)_3\dot{P}—Cl \qquad (7)$$

$$(ArO)_3\dot{P}—Cl + SCl_2 \longrightarrow (ArO)_3PCl_2 + ClS\cdot \qquad (8)$$

It is unlikely that active radical species such as chlorine atoms play an important role in these reactions. In this respect our proposal differs somewhat from that of Walling and Rabinowitz.[13]

A somewhat similar situation exists with sulfur monochloride when the following additional paths are necessary in the over-all reaction scheme

$$(ArO)_3\dot{P}Cl + S_2Cl_2 \longrightarrow (ArO)_3PCl_2 + ClS_2\cdot \qquad (9)$$

$$ClS_2\cdot + (ArO)_3P \longrightarrow (ArO)_3\dot{P}—S—S—Cl \qquad (10)$$

$$(ArO)_3\dot{P}—S—S—Cl \longrightarrow (ArO)_3P{=}S + ClS\cdot \qquad (11)$$

$$ClS\cdot + S_2Cl_2 \rightleftarrows SCl_2 + ClS_2\cdot \qquad (12)$$

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(1) A. C. Poshkus and J. E. Herweh, This Journal, **79**, 6127 (1957).

(2) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 325.

(3) (a) G. S. Harris and D. S. Payne, *J. Chem. Soc.*, 3038 (1956); (b) H. N. Rydon and B. L. Tonge, *ibid.*, 3043 (1956).

(4) (a) P. Rumpf, *Bull. soc. chim.* (*France*), 128C (1951); (b) A. E. Arbuzov and L. V. Nesterov, *Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk*, 427 (1954); *C. A.*, **49**, 9541*c* (1955).

(5) D. C. Morrison, This Journal, **77**, 181 (1955).

(6) (a) A. E. Arbuzov, B. A. Arbuzov, P. I. Alimov, K. V. Nikonorov, N. I. Rizpolozhenskii and O. N. Fedorova, *Trudy Kazan Filiala Akad. Nauk S.S.S.R., Ser. Khim. Nauk*, **2, 7** (1956); *C. A.*, **51**, 10363*g* (1957); (b) W. Lorenz and G. Schrader, German Patent 820,001 (1951).

(7) We have isolated and identified triethyl phosphorothionate and diethyl phosphorochloridate as the major reaction products of sulfur dichloride and triethyl phosphite.

(8) (a) E. E. Gilbert and C. J. McGough, U. S. Patent 2,690,450–1 (1954); (b) D. C. Morrison, *J. Org. Chem.*, **21**, 705 (1956); (c) K. A. Petrov, C. A. Sokolski and B. M. Polees, *Zhur. Obshch. Khim.*, **26**, 3381 (1956); *C. A.*, **51**, 9473*i* (1957).

(9) J. Michalski and J. Wieczorkowski, *Bull. Acad. Polon. Sci.*, Classe 3, 4279 (1956); *C. A.*, **51**, 4266*i* (1957).

(10) A. C. Poshkus and J. E. Herweh, This Journal, **79**, 4245 (1957).

(11) Investigations on the reactions of sulfonyl and sulfenyl chlorides with triaryl phosphites indicates that the reaction scheme proposed by Walling and Rabinowitz[13] may have to be modified to interpret our results. Details will be given in a forthcoming paper.

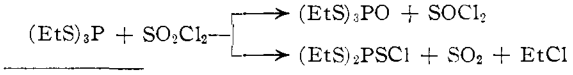
(12) The authors appreciate the opportunity one of us (A.C.P.) had to discuss the free radical chemistry of phosphorus with Drs. F. Ramirez and Cheves Walling.

(13) C. Walling and R. Rabinowitz, This Journal, **79**, 5326 (1957).

Sulfur–sulfur cleavage either heterolytically as proposed by Jacobsen, Harvey and Jensen[14] for reactions involving dialkyl disulfides and trialkyl phosphites or homolytically as interpreted by Walling and Rabinowitz[13] seems less attractive when sulfur monochloride is the reactant than the homolytic chain sequence we suggest. Cleavage at the Cl–S bond should proceed with a facility equal to that at the S–S bond since the Cl–S and S–S bond energies do not differ significantly.[15] Since the hindered phosphonyl radical is not expected to be highly reactive, steric considerations alone would point to an attack at the chlorine rather than the sulfur atom in the chain propagation step. Furthermore, the well-known fact that chlorine reacts only slowly with sulfur monochloride[16] also supports the contention that the reaction chain we propose for sulfur monochloride is a reasonable one.

Unlike reactions involving sulfur mono- or dichloride, those with sulfuryl or thionyl chloride are somewhat more complicated apart from the various consecutive reactions which may and, under suitable conditions, do occur. The most notable feature of these reactions is the oxygen transfer from the sulfur to the trivalent phosphorus atom. Our results in conjunction with the known reactions of phosphorus trichloride and sulfuryl[17] or thionyl chloride,[18] both known to be slow below 100° in absence of Lewis acids, and the more recent accounts on the reactions of sulfuryl chloride with diphenyl phosphorochloridite[19] and ethylphosphonous dichloride[20] lead to the generalization that compounds of type $(ArO)_nPCl_{3-n}$ and $R_nP\,Cl_{3-n}$ are readily oxidized by sulfuryl or thionyl chloride. In fact aryloxy groups seem to facilitate oxygen transfer and a halogen on the phosphorus atom is not necessary for the reaction to occur.

The behavior of the alkyl analogs to give sulfur dioxide, an alkyl halide and a dialkyl phosphorochloridate with sulfuryl chloride[1] thus differs from the aryl esters. Mixed aryl alkyl phosphites will react like trialkyl phosphites whereby the alkyl group is cleaved and the aryl group remains with the phosphorus moiety. The sulfur analogs of trivalent phosphorus acids behave somewhat similarly. We have found that trialkyl trithiophosphites react with sulfuryl chloride apparently along two simultaneous paths: one giving an oxidation product characteristic of triaryl phosphites and the other, like trialkyl phosphites, producing sulfur dioxide. This reaction, however, has not been worked out in sufficient detail for an extended discussion at this time. In contrast to our observations, Divinski and his co-workers[21] reported that thiophosphites do not undergo the Michaelis–Arbuzov reaction and mentioned the ease with which the phosphorus–sulfur bond is cleaved. Similarly, trialkyl[8a,22] and triaryl[10] phosphites as well as triaryl phosphines[23] deoxygenate sulfonyl halides. We have found that sulfur dioxide also is reduced by phosphites and we believe that sulfur trioxide or its adducts with tertiary amines or with ethers will be active oxidants for compounds of trivalent phosphorus.



$$(EtS)_3P + SO_2Cl_2 \left\{ \begin{array}{l} \longrightarrow (EtS)_3PO + SOCl_2 \\ \longrightarrow (EtS)_2PSCl + SO_2 + EtCl \end{array} \right.$$

When triphenyl phosphite is added to sulfuryl chloride in petroleum ether at low temperatures an immediate precipitate (or an emulsion if the reaction temperature is more than about 15°) forms. In order to ascertain whether this product was "triphenoxyphosphorus dichloride," triphenyl phosphite–sulfuryl chloride adduct or triphenyl phosphate, it was filtered off under anhydrous conditions at low temperatures and shown to be exclusively triphenyl phosphate. In media which are good solvents for triphenyl phosphate precipitation will not occur under similar conditions. A 1:1 mole ratio of the reactants gives practically theoretical yields of triphenyl phosphate; thionyl chloride can be recovered in good yields. Failure to observe a yellow color in the reaction mixture indicates the absence of sulfur dichloride which might be expected if the thionyl chloride formed deoxygenated easily. The argument that sulfur dichloride is not observed due to its rapid reaction with sulfuryl chloride is excluded because, although the equilibrium to give thionyl chloride is favored,[24] such a reaction in absence of catalysts is slow at temperatures prevailing under our conditions. A dilute solution of sulfur dichloride in sulfuryl chloride does not decolorize in the absence or presence of pyridine even after several hours at room temperatures. It is concluded that sulfuryl chloride is more reactive than thionyl chloride and if the reactions are conducted in an excess of sulfuryl chloride, side reactions due to participation of thionyl chloride can be reduced to negligible magnitudes.

Although these experiments normally were conducted in diffuse daylight augmented by fluorescent lighting, the same reactions occur in the dark as manifest by a rapid rise in temperature when the diluted reactants are mixed in absence of light. We conjecture that labile peroxidic intermediates formed by the action of oxygen on trivalent phosphorus compounds may be the source of initiating radicals. Despite the usual precautions to exclude air, traces of oxygen may have had access to the reaction mixture.

When sulfuryl chloride is added rapidly (with cooling) to triphenyl phosphite the results, not unexpectedly, are essentially the same as those for the reversed addition. However, when the sulfuryl chloride is added slowly to triphenyl phosphite, the

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[14] H. I. Jacobsen, R. G. Harvey and E. V. Jensen, THIS JOURNAL, **77**, 6064 (1955).

[15] T. L. Cottrell, "Strengths of Chemical Bonds," Butterworths, 1954, p. 258.

[16] N. V. Sidgwick, "Chemical Elements and Their Compounds," Vol. II, Oxford, 1950, p. 946.

[17] (a) R. Kirk and D. Othmer, "Encyclopedia of Chemical Technology," Vol. XII, Interscience Publishers, New York, N. Y., 1957, p. 410. (b) German Patent 415,315 (1921) as cited in Mellor, "Treatise of Inorganic and Theoretical Chemistry," Vol. X, Longmans, 1940, p. 657. (c) M. Trautz, as cited in Mellor, "Treatise on Inorganic and Theoretical Chemistry," Vol. X, Longmans, p. 674.

[18] H. B. North and J. C. Thomson, THIS JOURNAL, **40**, 774 (1918).

[19] H. R. Atherton, V. M. Clark and A. R. Todd, *Rec. trav. chim.*, **69**, 295 (1950).

[20] B. C. Saunders and T. S. Worthy, *J. Chem. Soc.*, 2115 (1953).

[21] A. F. Divinski, M. I. Kabachnik and V. V. Sidorenko, *Doklady Akad. Nauk S.S.S.R.*, **60**, 999 (1948); *C. A.*, **43**, 560*g* (1949).

[22] F. Hoffman, T. Moore and B. Kagan, THIS JOURNAL, **78**, 6413 (1956).

[23] L. Horner and H. Nickel, *Ann.*, **597**, 20 (1955).

[24] A. G. Evans and G. W. Meadows, *Trans. Faraday Soc.*, **43**, 667 (1947).

initial reduction of sulfuryl chloride is followed by further reduction of the resulting thionyl chloride according to equations 1, 2 and 3. Furthermore, an appreciable amount of sulfur dioxide is evolved and the solution assumes variable shades of yellow to red. The color indicates the presence of sulfur dichloride or monochloride in the reaction mixture.

Sulfur dioxide may arise from several sources: (a) by dissociation of the chlorosulfuryl radical believed to be a transient species in the reaction, (b) by reaction of sulfuryl chloride with triphenyl phosphorothionate and (c) during reactions involving thionyl chloride with triphenyl phosphite. The first possibility is excluded on the basis of experiments in which a mole equivalent of triphenyl phosphite reacted with one mole equivalent of sulfuryl chloride. Triphenyl phosphate was produced quantitatively and "triphenoxyphosphorus dichloride" was not formed as one would expect if sulfur dioxide were produced. This result also excludes any possibility of "triphenoxyphosphorus dichloride" as an intermediate which would react subsequently with sulfur dioxide. Although the reactions of sulfur dioxide with various chlorides of pentavalent phosphorus have been reported[19,25] we have found that the reaction with "triphenoxyphosphorus dichloride" is slow even at 25°. The second possibility is credible since we observed that triphenyl phosphorothionate reacts with sulfuryl chloride in ether at 20° (cooling necessary); the solution turns deep orange, sulfur dioxide can be detected, and triphenyl phosphate was isolated. Sulfur dichloride or monochloride, probably the main sulfur compounds formed, can account for the color. Thionyl chloride under similar conditions does not react with triphenyl phosphorothionate. The third possibility, which is probably the major source of sulfur dioxide as we have shown in our studies on thionyl chloride, will be discussed later in this paper.

In order to ascertain whether triphenyl phosphorothionate is oxidized by oxygen during its isolation

$$(\mathrm{PhO})_3\mathrm{PS} \xrightarrow{\mathrm{O}_2} (\mathrm{PhO})_3\mathrm{PO} + \mathrm{SO}_2$$

an ethereal solution of the phosphorothionate was shaken in air with alkaline aqueous alcoholic solution for 1–2 hours at room temperatures. Triphenyl phosphorothionate was recovered unchanged and neither sulfite nor sulfate were detected. Furthermore, it was found that although sulfur dioxide reduces trialkyl phosphites at an appreciable rate at 30° to give a mixture of the corresponding phosphate and phosphorothionate, at temperatures (<25°) used in these investigations triphenyl phosphite is not reduced to any appreciable extent. After several hours contact with sulfur dioxide at about 35°, triphenyl phosphite is recovered almost quantitatively and neither triphenyl phosphate nor triphenyl phosphorothionate was detected.

When triphenyl phosphite is added to sulfuryl chloride in proportions to satisfy the requirements of the reaction

$$4(\mathrm{PhO})_3\mathrm{P} + \mathrm{SO}_2\mathrm{Cl}_2 \longrightarrow 2(\mathrm{PhO})_3\mathrm{PO} + (\mathrm{PhO})_3\mathrm{PS} + (\mathrm{PhO})_3\mathrm{PCl}_2$$

sulfur dioxide is produced in variable amounts depending upon the reaction conditions. About 50 to 80% of the total sulfur is accounted for as triphenyl phosphorothionate and the remainder as sulfur dioxide. Surprisingly enough 10–20% of the sulfur is associated with "triphenoxyphosphorus dichloride."[26] The presence of a sulfur compound in the ether insoluble crystalline mass was somewhat disturbing, but an examination showed this to be most likely a solution of sulfur dioxide in "triphenoxyphosphorus dichloride." Analysis of this insoluble product after washing with dry ether showed that S:P:Cl = 1:5–6:6–7. Hydrolysis in cold dilute alkali converts up to 95% of the phosphorus compound into triphenyl phosphate. The acidified aqueous filtrate decolorizes an iodine solution,[27] the vapor decolorizes iodine paper, and on oxidation sulfate is produced. These results do not support thionyl chloride–triphenyl phosphite adducts such as those speculated by Bell[28] for alkyl analogs.

The low Cl:P ratio (1.2:1) compared to a theoretical value of 2:1 may be due to reactions involving triphenoxyphosphorus dichloride and triphenyl phosphite.[3b]

$$(\mathrm{PhO})_3\mathrm{PCl}_2 + (\mathrm{PhO})_3\mathrm{P} \longrightarrow (\mathrm{PhO})_4\mathrm{PCl} + (\mathrm{PhO})_2\mathrm{PCl}$$

Such a reaction would account for the appreciable presence of hydrolyzable chlorine compounds in the ether-soluble fraction. The extent of this reaction would depend upon the temperature to which the mixture is subjected and the promptness with which it is worked up. We have observed that the solid formed immediately after reaction becomes oily on standing in a dry atmosphere.

The ether-soluble components consist of triphenyl phosphate, triphenyl phosphorothionate and very likely both triphenyl phosphite and diphenyl phosphorochloridite. Trivalent phosphorus compounds are detected by decolorization of aqueous iodine solutions in both organic and water layers after sulfur dioxide has been removed by washing with dilute base, in the first case, and boiling the acidified aqueous washings in the second. Hydrolyzable halogen is present in considerable amounts (up to 50% of the available chlorine) most likely as the phosphorochloridite. This is consistent with the loss in weight of the oil on washing with dilute alkali. The hydrolysis of triphenyl phosphite[29] could not by itself account for this loss. A control consisting of triphenyl phosphate and phosphorothionate showed that these compounds could be recovered in better than 90% yield thus precluding loss of these constituents. The presence of the phosphorochloridite and the phosphite account for the high P:S ratio (1:4 to 1:6) which seems to be correlated roughly with the amount of sulfur dioxide formed

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(25) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 328.

(26) Triphenoxyphosphorus dichloride may be a mixture of products as Rydon has shown so nicely (Special Publ. No. 8 of Chemical Society, London). The melting points probably have little diagnostic value.

(27) It must be pointed out that triphenyl phosphite decolorizes aqueous iodine solutions quite readily, particularly on warming. The reaction is not as rapid as that with trialkyl phosphites or dialkyl phosphorous acid.

(28) A. Bell, U. S. Patent 2,508,364 (1950).

(29) (a) Noack, *Ann.*, **218**, 96 (1883); (b) A. E. Arbuzov and M. G. Imaev, *Doklady Akad. Nauk S.S.S.R.*, **112**, 856 (1957); *C. A.*, **51**, 13741.

(45–65% of the sulfuryl chloride used) in the reaction.

The reaction of sulfuryl chloride with triphenyl phosphite may proceed either through a cyclic transition intermediate proposed earlier for the reaction of sulfuryl chloride with trialkyl phosphite[1] or more likely, in this case, through relatively inactive radical intermediaries.

$$(PhO)_3P + ClSO_2\cdot \rightleftarrows (PhO)_3\dot{P}OSOCl \qquad (13)$$

$$(PhO)_3\dot{P}OSOCl \longrightarrow (PhO)_3PO + ClSO\cdot \qquad (14)$$

$$ClSO\cdot + SO_2Cl_2 \rightleftarrows SOCl_2 + ClSO_2 \qquad (15)$$

This reaction sequence is analogous to that reported for the radical initiated addition of sulfuryl chloride to olefins in presence of sulfur monochloride to give chlorosulfites.[30] Under our conditions the chlorosulfuryl radical neither dissociates into sulfur dioxide and chlorine nor does it transfer its halogen to other molecules. The attack of a phosphite molecule at an oxygen atom has been discussed by Ramirez and Dershowitz.[31] The ionic intermediate postulated by them resembles the one proposed in another paper.[1]

Thionyl chloride resembles sulfuryl chloride in its reaction toward triaryl phosphites or phosphines. A radical reaction path similar to that postulated for sulfuryl chloride interprets our results reasonably well.

$$(PhO)_3P + ClSO\cdot \rightleftarrows (PhO)_3POSCl \qquad (16)$$

$$(PhO)_3\dot{P}OSCl \longrightarrow (PhO)_3PO + ClS\cdot \qquad (17)$$

The chlorothiyl radical in competition with reaction 6 would abstract either a chlorine (equation 18) or an oxygen atom (equation 19) yielding in either case sulfur dichloride.

$$ClS\cdot + SOCl_2 \longrightarrow SCl_2 + ClSO\cdot \qquad (18)$$

$$ClS\cdot + OSCl_2 \rightleftarrows [ClSOSCl_2] \rightleftarrows ClSO\cdot + SCl_2 \qquad (19)$$

A yellow to orange discoloration of the reaction mixture sometimes observed indicates the presence of sulfur dichloride. Normally, the reaction solutions remain colorless or at most the oil which comes out is pale yellow with a greenish cast. The yellowish oil and the vapors above it oxidize iodide ions to iodine. When triphenyl phosphite reacts with a large excess of thionyl chloride, the reaction mixture turns a pale yellow and the major product is triphenyl phosphate. Only small amounts of triphenyl phosphorothionate and triphenoxyphosphorus dichloride roughly in a 1:1 mole ratio are formed. These results support the postulated reaction scheme.[32]

When thionyl chloride and triphenyl phosphite are reacting in a 1:3 mole ratio, the results are analogous to the reaction of sulfuryl chloride and triphenyl phosphite in a 1:4 mole ratio as one would expect. Sulfur dioxide is produced in variable amounts (20–40% of the thionyl chloride used). As in reactions involving sulfuryl chloride under analogous conditions, the sulfur dioxide appears to be dissolved in the "triphenoxyphosphorus dichloride" fraction, but most of it is lost when this is dried at low pressures. The manner by which sulfur dioxide is formed is not clear although the disproportionation of chlorothionyl radicals into sulfur dioxide and sulfur dichloride or reactions involving sulfur monoxide are likely sources.

The "triphenoxyphosphorus dichloride" fraction after being subjected to vacuum-drying showed only small amounts of sulfur. A phosphorus–chlorine ratio of 1.0:1.2 and the presence of phosphites as well as some chloride in the ether soluble portion indicates, as we have discussed above, that diphenyl phosphorochloridite and triphenyl phosphite are present.

A brief investigation on the reaction of thionyl chloride with triphenyl phosphine indicates a close similarity to the triphenyl phosphite reaction. Triphenyl phosphine oxide was identified and evidence for triphenyl phosphorus dichloride was found (hydrolyzable chlorine analysis). Triphenyl phosphine should be more suitable than triphenyl phosphite for studying oxygen transfer reactions since complex mixtures of phosphorus chlorides such as we experience in our work[3b] cannot form.

Experimental[3b]

Starting Materials.—Triphenyl phosphite (Eastman Organic Chemicals) was purified by washing its ethereal solution consecutively with 5% aqueous sodium hydroxide, distilled water and saturated aqueous sodium chloride. The ethereal solution dried over sodium sulfate was distilled, and the fraction boiling at 181–189° (1.0 mm.) was used in these reactions.

Both sulfuryl chloride and thionyl chloride (Eastman purified grade) were redistilled at atmospheric pressure and the fractions boiling at 69° and at 78°, respectively, were used in subsequent reactions.

Sulfur dichloride (Hooker Electrochemical Company) was redistilled under reduced pressures and the fraction boiling at 37–39° at 180 mm. was used.

All solvents used in these reactions were dried over sodium.

The Reaction of Triphenyl Phosphite with Sulfuryl Chloride. (a) Preliminary.—A solution of 45.9 g. (0.34 mole) of sulfuryl chloride in 24 ml. of benzene was added dropwise to a stirred solution of 93 g. (0.3 mole) of triphenyl phosphite in 77 ml. of benzene at 0°. After 15 hr. at ambient temperatures the orange colored 2-phase liquid reaction product was distilled at atmospheric pressure to remove low boiling components (pot temperatures 85°). The residual oil was distilled *in vacuo* to give 5 g. of an unidentifiable acidic forerun, b.p. 165–180° (1 mm.); 12 g. (0.045 mole) of diphenyl phosphorochloridate,[34] b.p. 180–182° (1 mm.); and 41 g. (0.13 mole) of triphenyl phosphate, b.p. 203–206° (1 mm.), which solidified on cooling. The white solid, m.p. 46–47°, reported m.p. 50°,[35] did not depress the m.p. of an authentic sample. The undistillable tarry residue gave no identifiable product, although phosphorus was shown to be present.

Some sulfur dioxide was evolved during the reaction. In subsequent experiments wherein sulfuryl chloride was added rapidly to triphenyl phosphite, diphenyl phosphorochlori-

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[30] (a) A. Y. Yakubovich and Y. M. Zinoviev, *J. Gen. Chem.* (*USSR*), **17**, 2028 (1947); *C. A.*, **43**, 1248i (1949); (b) M. S. Kharasch, *Inst. Intern. Chim. Solvay 8e Conseil Chim.*, 177 (1950); *C. A.*, **47**, 3253h.

[31] (a) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 856 (1957); (b) THIS JOURNAL, **78**, 5614 (1956).

[32] Evidence for sulfur monoxide as a reactive intermediate in reactions of thionyl chloride with trialkyl phosphites will be discussed in a subsequent paper.

[33] Boiling and melting points are uncorrected. Precautions were taken to exclude moisture and the reactions were conducted in a nitrogen atmosphere.

[34] Identified as the diphenyl-N-phenyl phosphoroamidate, m. p. 128–129°, and the N-benzyl phosphoroamidate, m.p. 100–102°, according to the procedure of A. B. Foster, W. G. Overend and M. Stacey, *J. Chem. Soc.*, 980 (1951).

[35] S. Sugden, J. B. Reed and H. Wilkins, *ibid.*, **127**, 1539 (1925).

date[36] was not obtained, the reaction mixture was not discolored, the yield of triphenyl phosphate was approximately 90%, indications were found for triphenyl phosphorothionate and the major portion of sulfuryl chloride was converted to thionyl chloride.

(b) **Mole Ratio 1:1.**—Triphenyl phosphite (41.5 g., 0.134 mole) in 30 ml. of petroleum ether (boiling range 30–60°) was added dropwise over a period of 1 hr. to a stirred solution of sulfuryl chloride (18.1 g., 0.134 mole) in 70 ml. of petroleum ether maintained at 5°. The reaction was moderately vigorous and an immediate turbidity developed (due to the formation of a white solid). The mixture of colorless solution and white solid[37] after 24 hr. under an atmosphere of nitrogen was stirred vigorously into 250 ml. of ice-cold 10% aqueous sodium hydroxide. The resultant white solid was filtered from the alkaline mixture, washed with cold water and dried *in vacuo* over P_2O_5. This product (40.6 g.; m.p. 47–50°) did not depress the melting point of authentic triphenyl phosphate. An additional quantity (1.8 g.; m.p. 42–48°) of triphenyl phosphate was recovered from the filtrate and washings. Thus, a total yield of 42.4 g. (97%) of triphenyl phosphate was recovered.

Only negligible amounts (about 0.1% of the total sulfuryl chloride used) of free sulfur dioxide were evolved during the reaction and detected in the exit gases (chlorine absent). The aqueous filtrate and washings after evaporation of petroleum ether were analyzed quantitatively for chloride, sulfite and sulfate by conventional analytical methods. Small amounts of sulfate (probably arising by air oxidation of the sulfite) were found. A sulfite–chloride ratio of 1:2 indicated that thionyl chloride had formed. In another run carried out in toluene, thionyl chloride, b.p. 75–80° at 747 mm. (reported[38] 78.8°), was isolated in 50% yields.

(c) **Mole Ratio 4:1.**—A solution of 31.3 g. (0.101 mole) of triphenyl phosphite in 30 ml. of petroleum ether was added dropwise over a period of 30 minutes to a stirred solution of 3.37 g. (0.025 mole) of sulfuryl chloride in 100 ml. of petroleum ether maintained at 5°. A white crystalline solid which precipitated initially turned into an immiscible pale yellow oil on continued addition of the reactant. The stirred reaction mixture was allowed to come to room temperature (45 minutes), and the clear colorless petroleum ether solution was decanted from the lower faintly yellow oily layer. The oil solidified on repeated washing with ethyl ether to leave behind 8.15 g. (86% yield) of hygroscopic white crystalline solid believed to be triphenoxyphosphorus dichloride,[39] m.p. 70–75°; reported[40] m.p. 80–81°. A mixture m.p. with an authentic sample showed no depression.

The petroleum ether layer and ethyl ether washings were combined and washed consecutively using 25-ml. portions: three times with cold 5% aqueous sodium hydroxide, twice with cold water and finally with saturated aqueous sodium chloride. The ethereal solution was dried and the solvents removed under reduced pressures (20 mm.). The resulting colorless oil (20.1 g.) was analyzed for sulfur (found 1.6% S). Triphenyl phosphorothionate, isolated from this mixture by chromatography over alumina, melted at 49–51°; reported[41] m.p. 53°. It did not depress the melting point of an authentic sample prepared according to the procedure given by Gottlieb,[42] but liquefied on mixing with triphenyl phosphate. Surprisingly enough triphenyl phosphate could not be eluted from the column even with such polar solvents as acetic acid.

Our failure to obtain the expected amount of sulfur in the material miscible in ether prompted a repetition of the experiment using twice the amount of reagents. Effluent gases and low boiling distillate (pot temperatures <50°) were washed with dilute sodium hydroxide. Qualitative tests indicated only traces of sulfate and chloride. Quantitative analysis showed that 0.0121 mole of sulfur dioxide (equivalent to 24% of the sulfuryl chloride used) were removed. The still residue was separated into ether-soluble (52.1 g.) and ether insoluble (15.7 g.) portions. The ether insoluble product was analyzed. Found: P, 6.9; Cl, 10.2; S, 1.5. Hydrolysis of 11.9 g. of this solid with excess cold 5% aqueous sodium hydroxide and extraction of the hydrolyzate with ether gave 8.1 g. of triphenyl phosphate (m.p. 48–50° with no depression in melting point of authentic sample); thus 95% of the total phosphorus compounds was converted into and recovered as triphenyl phosphate. The aqueous extracts showed the presence of phenol (0.024 mole) and sulfur dioxide; only traces of sulfate detected.

The ether-soluble portion of the reaction mixture was analyzed. Found: P, 9.9; Cl, 2.4; S, 1.6. An ethereal solution of the oil was washed with dilute base and the resultant product (46.6 g.) after removal of ether analyzed. Found: P, 9.4; Cl, 0.7; S, 1.5. Triphenyl phosphite (or at least a phosphite) was detected by decolorization of an iodine solution. The oil on standing developed hydrogen chloride presumably by slow hydrolysis of residual acid chlorides. The aqueous washings showed presence of small amounts of sulfite and phenol; phosphites were present.

The Reaction of Triphenyl Phosphite with Thionyl Chloride. (a) **Mole Ratio 3:1.**—Triphenyl phosphite (23.6 g., 0.076 mole) in 35 ml. of petroleum ether was added dropwise in 20 minutes to a stirred solution of 2.97 g. (0.025 mole) of thionyl chloride in 75 ml. of petroleum ether maintained at 5°. When the reaction mixture reached ambient room temperatures (about 30 minutes), two layers were observed—a clear colorless solvent layer and an immiscible milky white oil. The procedure used in working up the reaction product was essentially that followed in the reaction of the phosphite with sulfuryl chloride. "Triphenoxyphosphorus dichloride" (fraction 9.21 g., m.p. 75–80° with some softening at 55°) was isolated; it did not depress the m.p. of an authentic sample of the dichloride. The solvent layer gave 14.2 g. of a turbid colorless oil which analyzed 4.5% sulfur. A sample of this oil (1.0 g.) was taken up in petroleum ether and chromatographed on an alumina column to give 0.4 g. of triphenyl phosphorothionate (m.p. 48–50°; no depression in m.p. with known sample). Triphenyl phosphate could not be removed from the column as mentioned previously and as we have found in control runs.

In another run using the same procedure and quantities, 9.2 g. of the resulting hygroscopic solid was dried several hours at about 1 mm. at ambient room temperatures and analyzed. Found: P, 7.01; Cl, 9.1; S, none. Variable amounts of sulfur are present if the sample is inadequately "dried." The ether-soluble fraction after washing with cold dilute aqueous sodium hydroxide and drying gave 13.9 g. of an oil which was analyzed. Found: P, 9.4; S, 3.14; Cl, 0.92. This oil decolorized an aqueous iodine solution. Sulfur dioxide was found in the aqueous washings.

(b) **Excess Thionyl Chloride.**—A solution of 6.2 g. (0.02 mole) of triphenyl phosphite in 20 ml. of petroleum ether was added over a period of 1 hr. to a vigorously stirred solution of 37.9 g. (0.2 mole) of thionyl chloride in 50 ml. of petroleum ether at 0°. An immediate turbidity appeared in the otherwise colorless solution. The amount of immiscible pale yellow oil increased during the course of the reaction.

The volatile products (mainly petroleum ether and thionyl chloride) were distilled at 20 mm. with the pot temperature maintained at about 40°. Thionyl chloride was removed from the residual oil by adding 25 ml. of petroleum ether and distilling; this process was repeated. Ethyl ether (60 ml.) was then added to the residual oil. More

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(36) Diphenyl phosphorochloridate was formed by the thermolysis of triphenoxyphosphorus dichloride during distillation. It was demonstrated that after refluxing an equimolar mixture of triphenyl phosphate and sulfuryl chloride in petroleum ether for 2.5 to 3 hr., the former was recovered unchanged.

(37) The solid liquefied on warming to ambient temperatures to yield an immiscible oil. A small portion of this oil was removed, crystallized by cooling and washed with petroleum ether. These operations were carried out under anhydrous conditions to preclude any hydrolysis of the dichloride or adduct. These precautions proved unnecessary since the solid was found to be triphenyl phosphate (m.p. 46–49°, no depression in mixture m.p. with an authentic sample of triphenyl phosphate). In later experiments the low boiling components were removed at low pressure (pot temperature <60°) to leave behind almost a quantitative yield of triphenyl phosphate which melted at 48–50° without any purification.

(38) N. A. Lange, "Handbook of Chemistry," 8th Ed., Handbook Publ., Sandusky, Ohio, 1952.

(39) The isolation of triphenoxyphosphorus dichloride was carried out in a dry-box and all m.p.s were taken in sealed tubes.

(40) D. G. Coe, S. R. Landauer and H. N. Rydon, *J. Chem. Soc.*, 2281 (1954).

(41) Autenrieth and Hildebrand, *Ber.*, **31**, 1094 (1898).

(42) H. B. Gottlieb, THIS JOURNAL, **54**, 748 (1932).

than half of the oil went into solution. The ethereal layer was decanted; further addition of ethyl ether to the immiscible oil caused a white solid to come out. This was dried under vacuum and was shown to be triphenoxyphosphorus dichloride (yield 0.4 g., 0.001 mole) by its m.p. 74–79° (incipient sintering at 60°) and failure to depress the m.p. of an authentic sample of the dichloride.

The ethereal extracts (about 150 ml.) were combined and washed consecutively with three 15-ml. portions of cold 10% aqueous sodium hydroxide and cold water and finally with a saturated aqueous salt solution. The washings were shown to be free from phenol by testing with bromine water. The ethereal solution (dried over sodium sulfate) was distilled under reduced pressures (water aspirator) to remove low boiling components. After several days the colorless oil (5.2 g.) partially solidified and no phenolic odor could be detected. The crystals were filtered and washed with small portions of cold petroleum ether to give 1.2 g. (0.0037 mole) of triphenyl phosphate melting at 46–50°. The oily filtrate was taken up in 200 ml. of petroleum ether and chromatographed on an alumina column. Triphenyl phosphorothionate (0.7 g., 0.002 mole) was recovered and identified by its melting point and mixture melting point.

The Reaction of Triphenyl Phosphite with Sulfur Dichloride.—A solution of triphenyl phosphite 15.8 g. (0.051 mole) in 25 ml. of petroleum ether was added slowly to a stirred solution of sulfur dichloride 2.58 g. (0.025 mole) in 50 ml. of petroleum ether maintained at 10°. The amount of a yellow solid initially formed on the walls of the reaction flask increased with further addition of the phosphite, while the initial red color of the solution was discharged gradually. The reaction mixture consisting of a white crystalline solid suspended in the turbid solution was now allowed to reach ambient temperatures. After 24 hours under an atmosphere of dry nitrogen, ethyl ether was added and the clear solution was decanted from the highly hygroscopic white solid. The solid product was washed with several portions of ethyl ether and dried under vacuum; yield 7.34 g. (77%); m.p. 70–75°. A mixture m.p. with an authentic sample of triphenoxyphosphorus dichloride gave no depression.

The ether washings and mother liquor were combined and washed consecutively using 15-ml. portions: four times with cold 5% aqueous sodium hydroxide solution, three times with cold water and once with a saturated sodium chloride solution. The resulting solution was dried over anhydrous sodium sulfate; and the ether, removed under reduced pressure (water aspirator), left a turbid oily residue which crystallized to an oily solid (8.7 g.).[43] Recrystallization from aqueous alcohol (75%) gave 7.5 g. (88% yield) of a white solid, m.p. 49–50°; reported m.p. for triphenyl phosphorothioate 50°. The melting point of authentic triphenyl phosphorothionate was not depressed although the solid gave an oil at room temperatures with triphenyl phosphate.

The Reaction of Triphenyl Phosphite with Sulfur Monochloride.—Sulfur monochloride was prepared by passing dry chlorine into sulfur heated above its melting point. The sulfur monochloride formed was condensed and collected in a receiver. The crude reaction product was distilled at atmospheric pressures and the fraction boiling at 132°[44] was used in the following reaction.

Triphenyl phosphite (23.6 g., 0.076 mole) in 25 ml. of petroleum ether was added dropwise in 20 minutes to a stirred solution of 3.37 g. (0.025 mole) of sulfur monochloride in 50 ml. of petroleum ether maintained at 10°. An immediate reaction occurred to give a turbid reaction mixture. When the reaction mixture reached room temperatures, it separated into a slightly turbid colorless solvent layer and a pale yellow solid. The reaction mixture was transferred to a dry-box and the solution carefully decanted from the solid which was washed with several portions of ethyl ether. After drying under a vacuum, the white crystalline solid (8.2 g., 86% yield) melted at 69–74° (reported m.p. 80°) and did not depress the melting point of authentic triphenoxyphosphorus dichloride.

The combined supernatant petroleum ether and ether washings were washed consecutively with 10-ml. portions of 5% aqueous sodium hydroxide (three times), water (two times) and finally with a saturated sodium chloride solution. The organic layer was dried over anhydrous sodium sulfate and the solvents removed under reduced pressure (water aspirator) to leave an oil which crystallized on cooling. This crude white product 14.2 g. (82.5% yield) was recrystallized from 75% alcohol to give 12 g. of triphenyl phosphorothionate (m.p. 49–51°; reported m.p. 50°).

The Reaction of Triphenyl Phosphine with Thionyl Chloride (Mole Ratio 1:2).—A solution of 13.1 g. (0.05 mole) of triphenyl phosphine,[45] [the fraction, b.p. 162–166° (0.5 mm.), m.p. 74–80° (reported b.p. 188° (1 mm.), m.p. 79°) was used in this work] in 75 ml. of benzene was added over a period of 30 minutes to 12.0 g. (0.10 mole) of thionyl chloride in 25 ml. of benzene. The reaction was not vigorous and gave a mixture that separated into two yellow layers. The upper benzene layer was distilled under reduced pressure (water aspirator) to leave an amber colored semi-solid mass which reacted violently with aqueous sodium hydroxide. The semi-solid product was treated with an excess of 5% sodium hydroxide solution. The resulting water-insoluble straw-colored solid was extracted with ether, the combined ether extracts were washed with water and dried over anhydrous sodium sulfate. Distillation of the ether under reduced pressure (water aspirator) left 7.7 g. of a white solid which, when recrystallized from heptane, melted at 153–156°; reported for triphenyl phosphine oxide, m.p. 153°.[46] A mixture m.p. with an authentic sample[47] of the phosphine oxide showed no depression.

A portion of the benzene insoluble layer (14.2 g.) after washing with several portions of benzene was added to water (violent reaction), and the water-immiscible oil formed was extracted with ether to remove triphenyl phosphine oxide. The immiscible oil was analyzed for hydrolyzable chlorine. *Anal.* Calcd. for $(C_6H_5)_3PCl_2$: Cl, 21.3. Found: Cl, 24.0. The product obviously was impure for triphenyl phosphorus dichloride has a reported m.p. 176°.[48]

The Reaction of Triphenyl Phosphorothionate with Sulfuryl Chloride.—When a solution of 17.1 g. (0.05 mole) of triphenyl phosphorothionate[33] in 50 ml. of ethyl ether was added to a solution of 13.5 g. (0.1 mole) of sulfuryl chloride in 10 ml. of ethyl ether, cooling was necessary to maintain the temperature at 20–25°. The orange-red reaction mixture was allowed to stand overnight; any gases formed were swept out by a slow stream of nitrogen and scrubbed through a 5% sodium hydroxide solution. The reaction mixture became lighter in color (orange) and a small amount of elemental sulfur had collected at the base of the sintered glass bubbler leading into the alkaline solution. These observations together with the odor of the reaction mixture strongly suggest the presence of sulfur dichloride. The solvent and other low boiling components were distilled under reduced pressure (water aspirator) in an atmosphere of nitrogen. The low boiling distillate was collected in a Dry Ice trap followed by a trap containing 5% sodium hydroxide solution. The residual yellow oil solidified after some time. The volatile acidic products were removed by adding ether and distilling. The resulting white solid was filtered, washed with several portions of cold petroleum ether and shown to be triphenyl phosphate (yield 12.4 g., m.p. 49–50°). Upon concentrating the petroleum ether washings, a second crop of triphenyl phosphate (2.7 g., m.p. 49–50°) was obtained. Evaporation of petroleum ether from the filtrate yielded a yellow semi-solid product (1.3 g.) having a pungent odor and believed to be a mixture of the phosphate and phosphorothionate.

A qualitative colorimetric examination of the orange colored condensate (approximately 100 ml.) obtained in the Dry Ice trap indicated the presence of about 3 g. of sulfur dichloride.

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(43) This material undoubtedly contains a small amount of triphenyl phosphate resulting from decomposition of the dichloride.

(44) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. X, Longmans, 1940, p. 633.

(45) (a) H. Gilman and C. C. Vernon, THIS JOURNAL, **48**, 1063 (1926); (b) P. Walden and R. Swinne, *Z. physik Chem.*, **79**, 714 (1912).

(46) Michaelis and Soden, *Ann.*, **229**, 295 (1885).

(47) Triphenyl phosphine oxide was prepared by oxidizing a glacial acetic acid solution of the corresponding phosphine with 30% hydrogen peroxide; after standing several days at ambient temperatures, the reaction product was worked up to yield a white solid, m.p. 154–156°.

(48) V. Grignard and J. Savard, *Compt. rend.*, **192**, 592 (1931).

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Lancaster, Pennsylvania

[Contribution from the Dow Chemical Company]

Exchange Properties of the Tetracyanonickelate Ion with Certain Amino Acid Complexes of Nickel(II)[1-3]

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The manner in which nickel in the tetracyanonickelate ion, $Ni(CN)_4^{-2}$, exchanges with nickel in each of four amino acid complexes of the metal has been studied employing radioactive nickel tracer. Poor correlation is exhibited between exchange rate and charge of the amino acid complex. In exchanges between strong and weaker complexes, the specific nature of the weaker complexing agent affects the exchange rate more than does the charge of the resulting complex. Reactions are first order in respect to each of the exchanging species, suggesting as the most probable reaction mechanism a direct transfer of nickel atoms resulting from bimolecular collision. Exchange rate, activation energy and entropy of activation were calculated for each exchange.

Introduction

Long has reported[4] a good correlation between the rate of exchange of nickel between two nickel complexes and the respective charges of the complexes involved, more rapid exchanges taking place between species of opposite charge than between species of like charge. In the work reported here the manner in which nickel tied up in the tetracyanonickelate ion exchanges with that associated with four amino acid complexes of the metal was studied. Since simple amino acid complexes of nickel can be obtained as cationic, anionic or neutral species, depending upon the particular amino acid used, these complexes are useful in studying the effect of the charge borne by the weaker complex upon the rate of exchange of its nickel with that of the tetracyanonickelate ion.

Experimental

Radionickel.—In each of the exchange reactions one of the nickel complexes, usually the amino acid complex, was made up using nickel containing a little radioactive nickel-63. One of the complexes was isolated at the end of the exchange period and its nickel electroplated on a copper planchette. Determination of the change in specific activity of the nickel associated with this complex provided a convenient measure of the extent of exchange. Radionickel used in these experiments was obtained from the United States Atomic Energy Commission, Oak Ridge, Tennessee. Cobalt activity present in the original metal was removed by repeated dimethylglyoxime precipitation of the nickel using "cold" cobalt carrier.

Counting Infinitely Thick Radionickel Plates.—The electroplated nickel was "infinitely thick" in respect to the weak Ni^{63} β-radiation. The unavoidable presence of long-lived Ni^{59}, whose decay is accompanied by the emission of X-rays, causes the counting rate for nickel of a given specific activity to increase with thickness even beyond infinite thickness. To determine accurately the specific activity of the plated nickel it was necessary to keep the weight of these plates nearly constant.

Preparation of Nickel Complexes. Potassium Tetracyanonickelate.—This compound was prepared from nickel of natural isotopic composition using the procedure described in "Inorganic Syntheses."[5] Analysis of crystals of this salt for nickel gave 23.8% by both the dimethylglyoxime precipitation method[6] and by titration with Versene.[7] The theoretical amount of nickel in $K_2Ni(CN)_4 \cdot H_2O$ is 22.7%. In the analysis for cyanide, weighed, acidified samples were steam distilled and the hydrocyanic acid caught in 0.1 *N* sodium hydroxide solution. The cyanide was titrated with standard silver nitrate solution according to the method described by Kolthoff and Sandell.[8] The average value obtained was 41.7%. The molar ratio of nickel to cyanide is therefore 1.00/3.96 which is within the experimental error of the theoretical value of 1.00/4.00. A standard solution of potassium tetracyanonickelate was prepared.

Amino Acid Complexes.—The amino acid complex solutions were prepared by adding to the required amount of a standard solution of hot nickel sulfate an amount of amino acid calculated to form a 2:1 complex of all of the nickel present. The *p*H of the solution was raised to 9 by the addition of sodium hydroxide solution. The absence of nickel hydroxide precipitate in these solutions, even on long standing, precludes the presence of uncomplexed nickel. In the kinetic study, nickel did tend to precipitate from the more dilute solutions. To prevent this, twice the theoretical amount of glycine was employed in the tetracyanonickelate–nickel glycinate series and three times the theoretical amount of glutamic acid was used in the tetracyanonickelate–nickel glutamate series. Thus the amino acid was present in known and constant excess.

Nickel Versenate.—A standard nickel Versenate solution was prepared by adding to a known amount of cold nickel sulfate in solution a calculated amount of recrystallized disodium Versenate.

Tris-ethylenediamine–Nickel.—A solution of this complex was prepared using a measured quantity of standard hot nickel sulfate solution and a slight excess of redistilled ethylenediamine. The *p*H of the solution was raised to 9 by the addition of sodium hydroxide solution.

Nickel Tetramine.—This complex was prepared using a measured quantity of standard hot nickel sulfate solution and excess ammonium hydroxide.

Procedure Used in Exchange Experiments.—The exchange reactions were carried out in reaction vessels having the shape of an inverted "V" with a ground glass stoppered opening at the apex. Each of the two complex solutions, at twice the desired final concentration, was placed in one

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[3] This work was assisted in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

[4] F. A. Long, This Journal, **73**, 537 (1951).

[5] W. C. Fernelius, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 227–228.

[6] F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, 9th Ed., John Wiley and Sons, Inc., New York, N. Y., 1942, p. 193.

[7] G. Schwarzenbach, "Titration Methods Using Complexons."

[8] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis, The Macmillan Co., New York, N. Y., 1948, p. 478.