I were obtained. They are essentially the same as those obtained with the inert gases. Thus the total pressures of any complexes of NH_3 with $ZnCl_2$ were less than 5% of the pressure of the $ZnCl_2$ itself.

An upper limit to the heat of the reaction

$$ZnCl_2(g) + NH_3(g) = ZnNH_3Cl_2(g)$$

can be estimated to be about 3 kcal. based on an estimate of -20 e.u. for the entropy (approximately a Trouton rule value) and an equilibrium constant of less than 0.05 atm.$^{-1}$ for the reaction.

The production and transport of NH_4Cl in the experiments with NH_3 carrier gas can be accounted for as follows. Ammonolysis of the liquid $ZnCl_2$ in the sample container probably occurred.

$$NH_3(g) + ZnCl_2(l) = HCl(g) + Zn(NH_2)Cl \text{ (dissolved in } ZnCl_2)$$

This is quite comparable to the hydrolysis of $ZnCl_2$ and similar salts, which makes them difficult to purify.

$$H_2O(g) + ZnCl_2(l) = HCl(g) + Zn(OH)Cl \text{ (dissolved in } ZnCl_2)$$

The HCl so produced was carried by the NH_3, probably as HCl since NH_4Cl is dissociated[5] in the gas phase. The NH_3 stream also carried the saturation pressure of $ZnCl_2$. In the cold collector tube the $ZnCl_2$ condensed with some ammonia of crystallization and the HCl as NH_4Cl since the gas stream contained excess NH_3.

It is probable that the results in the older literature[2] are to be explained as above rather than as evidence for a gaseous complex.

[5] See N. V. Sidgwick, "The Chemical Elements and their Compounds," Vol. 1, Oxford, England, 1950, p. 661.

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The Reduction of Nickel(II) Halides by Trialkyl Phosphites

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We have found that nickel(II) halides are reduced by trialkyl phosphites in the presence of an amine to form the tetrakis(trialkyl phosphite)nickel(0) complexes. Previously, $Ni[P(OC_2H_5)_3]_4$ had been prepared by refluxing $Ni(CO)_4$ and $(C_2H_5O)_3P$ until CO had been completely evolved.[1] The proposed stoichiometry for the new preparation is

$$NiX_2 + 5(C_2H_5O)_3P + 2R_3N + H_2O \longrightarrow Ni[P(OC_2H_5)_3]_4 + 2R_3NHX + (C_2H_5O)_3P{=}O$$

By this reaction trimethyl phosphite and triethyl phosphite yield nicely crystalline nickel(0) compounds, but tributyl phosphite and triphenyl phosphite give poorly defined products. $NiCl_2 \cdot 6H_2O$, $NiBr_2$, and NiI_2 (prepared from $Ni(NO_3)_2 \cdot 6H_2O$ and NaI in absolute ethanol) have been successfully utilized. Triethylamine, diethylamine, monoethylamine, and aqueous ammonia have been successful as bases. Water, methanol, ethanol, or acetonitrile may be used as solvents; the best crystals form in acetonitrile.

Experimental

Typically, $Ni[P(OC_2H_5)_3]_4$ may be prepared in the following manner. Dissolve 0.5 g. of $NiBr_2$ in 10 ml. of warm acetonitrile, cool, and filter through a medium glass frit. Add 1.6 ml. of triethyl phosphite to the solution, following with the dropwise addition of 0.5 ml. of diethylamine. When the color of the solution fades to a light pink or yellow-green, the solution is cooled. The resulting crystals are filtered and washed with cold methanol until all trace of color has been removed; yield 30%; m.p. 108°, lit.[1] 107°.

Anal. Calcd. for $C_{24}H_{60}O_{12}P_4Ni$: C, 39.83; H, 8.30; Ni, 8.16; P, 17.15. Found: C, 39.41; H, 8.26; Ni, 8.24; P, 17.28.

The pure white crystals are insoluble in water, slightly soluble in methanol, and very soluble in most nonpolar organic solvents. Tetrakis(triethyl phosphite)nickel(0) is more stable with respect to decomposition than the trimethyl phosphite compound.

The ammonium salt produced by the reaction may be isolated as a white crystalline solid by the addition of ethyl ether to the reaction vessel immediately after mixing the reactants. The ammonium salt is identified by solubility, melting point, and infrared spectrum. Evidence for the existence of triethyl phosphate in the reaction mixture was obtained by v.p.c. analysis using a 6-ft. column of 1.5% silicone oil on glass beads. The reaction mixture produced one more fraction than did a similar mixture without the nickel salt. This additional peak appeared with identical retention time when $(C_2H_5O)_3P{=}O$ was added to the blank solution, and the effluent gas condensed onto NaCl plates exhibited the infrared spectrum of the tetraethyl ester of pyrophosphoric acid (Sadler Midget Index No. 78B), indicating a reaction at elevated temperature.[2]

Results

The molecular weight of $Ni[P(OC_2H_5)_3]_4$ in freezing benzene was found to be less than the monomer weight of 723 and dependent upon the solution concentration. Six different determinations showed a nearly linear decrease of the apparent molecular weight with a decrease of concentration (apparent molecular weight, molality: 657, 0.0438; 624, 0.0366; 611, 0.0314; 585, 0.0199; 574, 0.0166; 552, 0.0142). Assuming an equilibrium involving only tricoordinate Ni(0)[3]

$$Ni[P(OC_2H_5)_3]_4 \rightleftharpoons Ni[P(OC_2H_5)_3]_3 + P(OC_2H_5)_3$$

these data correspond to a dissociation of 10–31%. The calculated molal "equilibrium constant" for the above dissociation increases from 5 to 20 $\times$ 10^{-4} as the concentration decreases. This is significantly smaller than the apparent dissociation of the tetrakis(triphenyl phosphite)palladium(0), where the dissociation also seems to involve a second ligand.[4]

A nickel hydride species was rejected on the basis of the reaction with I_2 in pyridine and the infrared spectra.

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[1] J. R. Leto and M. F. Leto, *J. Am. Chem. Soc.*, **83**, 2944 (1961).

[2] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 340.

[3] L. S. Meriwether and M. L. Fiene, *J. Am. Chem. Soc.*, **81**, 4200 (1959).

[4] L. Malatesta and M. Angoletta, *J. Chem. Soc.*, 1186 (1957).

Reaction of $Ni[P(OC_2H_5)_3]_4$ with I_2 in pyridine in a closed, evacuated flask released no gas. Determination of excess I_2 in the pyridine after this reaction showed that 5 moles of I_2 per mole of $Ni[P(OC_2H_5)_3]_4$ was used. Known bis(triphenylphosphine)platinum hydride, $[(C_6H_5)_3P]_2PtH_2$, exhibits infrared M–H stretching bands at 1670 and 815 cm.$^{-1}$.[5] The infrared spectra of tetrakis(triethyl phosphite)nickel(0) in Nujol and in a KBr pellet are practically identical with the spectrum of purified triethyl phosphite over the range 4000 to 670 cm.$^{-1}$ showing no indication of M–H stretching frequencies. The most plausible equation which fits this stoichiometry is

$$Ni[P(OC_2H_5)_3]_4 + 5I_2 \longrightarrow NiI_2 + 4(C_2H_5O)_3PI_2$$

We anticipate that this new preparation will provide a more convenient route to other Ni(0) complexes and will help clarify aspects of other reactions involving Ni(II) organophosphorus complexes.

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[5] L. Malatesta and R. Ugo, *J. Chem. Soc.*, 2080 (1963).

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Synthesis of Nitrogen Trifluoride from the Elements

BY WALTER MAYA

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It has been reported that nitrogen trifluoride cannot be synthesized from the elements by the action of an electrical discharge at low temperatures.[1] We have found that nitrogen trifluoride can be synthesized in substantial yields by the action of an electrical discharge at liquid nitrogen temperature on a gaseous mixture of fluorine and nitrogen. The synthesis of nitrogen trifluoride appears analogous to the synthesis of fluorine oxides from the elements under essentially the same conditions.[2,3] However, unlike the fluorine oxides, variations of the stoichiometry of the fluorine–nitrogen mixtures did not lead to other nitrogen–fluorine compounds such as N_2F_2.

Experimental

A 15-kv., 30-ma. luminous tube transformer was used as the power source for the discharge. The discharge cell consisted of a glass U-tube, with each leg of the U equipped with copper electrodes. The electrodes were 8 cm. apart. The whole cell was immersed in liquid nitrogen during the discharge. A mixture of fluorine and nitrogen was prepared by admitting the requisite amount of gas into an evacuated 2-l. glass bulb; the fluorine is storable in glass for days, if the glass is thoroughly dry. Mixtures of the two gases investigated were 25% F_2, 75% N_2 and 75% F_2, 25% N_2. The best yields of NF_3 were obtainable with the latter mixture. The gaseous mixture was admitted into the discharge cell at a rate that allowed the pressure in the cell to remain between 20 and 40 mm. After leaving the discharge cell, the noncondensable gases were pumped off through a bubbler manostat filled with Fluorolube oil, through a fluorine absorber made of sodium chloride–soda lime, and to a vacuum pump.

At the end of the reaction, the discharge cell was allowed to warm gradually to room temperature, and its contents were fractionated in a high-vacuum line by pumping through a −196° and a −210° (solid nitrogen) trap. In the latter trap, nitrogen trifluoride in yields of 30% was found. The NF_3 was characterized by infrared[4] and mass spectra.

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[1] O. Ruff and J. Zedner, *Ber.*, **42**, 1037 (1909).

[2] O. Ruff and W. Menzel, *Z. anorg. allgem. Chem.*, **211**, 204 (1933).

[3] A. V. Grosse, A. G. Streng, and A. D. Kirshenbaum, *J. Am. Chem. Soc.*, **83**, 1004 (1961).

[4] J. H. Simons, Ed., "Fluorine Chemistry," Academic Press Inc., Vol. II, New York, N. Y., 1954, p. 498.

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Matrix Isolation Spectra of $HBCl_2$ and $DBCl_2$

BY C. D. BASS, L. LYNDS, T. WOLFRAM, AND R. E. DEWAMES

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In a recent paper, DeWames and Wolfram have developed a method of vibrational analysis of substituted and perturbed molecules utilizing the Green's function and partitioning techniques.[1] We have applied this method to planar XY_3 molecules and calculated the spectra of $HBCl_2$ and $DBCl_2$ from the observed frequencies of BCl_3, without invoking a force constant model.[2] Since the gas phase spectra of $HBCl_2$ and $DBCl_2$ are complicated by interference from BCl_3, which cannot be eliminated,[3] we obtained the matrix isolation spectra of $HBCl_2$–BCl_3 and $HBCl_2$–$DBCl_2$–BCl_3 mixtures in a large excess of argon at $\approx$ 10°K.[4] Although the matrix spectra are also quite complex, they have provided us with additional evidence in support of our gas phase calculations and assignments, as well as showing some interesting features.

Figure 1 shows some of the typical matrix isolation spectra which were observed. Table I lists the results of our calculations, and the gas phase assignments. The following correlations from the $HBCl_2$–BCl_3 spectrum are immediately apparent: a triplet with peaks at 2647, 2639, and 2625 cm.$^{-1}$ in the region where the B–H stretching band is observed (2617 cm.$^{-1}$); two bands at 1116 and 1099 cm.$^{-1}$, which are near the frequencies of the B^{10} and B^{11} components of the B–Cl asymmetric stretch (1100 and 1089 cm.$^{-1}$); and a doublet centered at 895 cm.$^{-1}$, which correlates with the frequency assigned to the B^{11}–H in-plane deforma-

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[1] R. E. DeWames and T. Wolfram, *J. Chem. Phys.*, **40**, 853 (1964).

[2] C. D. Bass, L. Lynds, T. Wolfram, and R. E. DeWames, *ibid.*, in press.

[3] $6HBCl_2 \rightleftarrows 4BCl_3 + B_2H_6$.

[4] G. C. Pimentel, *Spectrochim. Acta*, **12**, 94 (1958).