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Effect of Carrier Gas on the Transpiration of Zinc Chloride[1]

BY DANIEL CUBICCIOTTI

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There are reports in the older literature[2] that $Zn(NH_3)Cl_2$ is stable enough to be distilled. That is, presumably the zinc ammonia complex is stable in the gas phase. A calculation of the upper limit for the energy of addition of an NH_3 to a gaseous $ZnCl_2$ molecule can be made using the approach and the parameters given by Basolo and Pearson[3] for the solvation of gaseous ions. Their treatment was modified to the present case by taking into account the negative ions, assumed to form a linear, symmetrical $ZnCl_2$ molecule. The upper limit to the energy of association, obtained when the NH_3 molecule was placed as close as ionic radii would allow to the Zn, was about 35 kcal. Thus it seemed reasonable to look for the gaseous complex molecule.

Such a gaseous complex would manifest itself as an apparent increase in the vapor pressure of zinc chloride in a transpiration experiment with ammonia as the carrier gas. Accordingly, transpiration experiments were made with several different carrier gases, some inert (N_2, He. SF_6) and some possibly reactive (NH_3, HCl). In all these experiments, the apparent vapor pressure of the zinc chloride was essentially the same. Thus we found no evidence for gaseous complexes with HCl and NH_3 and no effect with inert carrier gases having molecular weights that differ as much as those of He and SF_6.

The experimental arrangement was the same as that described earlier,[4] except that when HCl or NH_3 was used as a carrier gas, the amount of gas passed was determined by absorbing it in known amounts of base or acid solutions and back-titrating. The containers were fused quartz. The agreement of the pressures measured at different flow rates (fourfold change for N_2 and twofold for He—see Table I) indicates that the gas stream was saturated and diffusion was negligible in these experiments.

TABLE I

VAPOR PRESSURE OF $ZnCl_2$ IN VARIOUS GASEOUS ATMOSPHERES

Gas (1 atm. total press.)	Flow rate, cc./min.	Temp., °C.	P ($ZnCl_2$), mm.	P ($ZnCl_2$), mm., cor. to 393.3°	(av.)
N_2	5	389.4	0.378	0.432	0.438
	12	388.1	0.368	0.447	
	21	387.1	0.351	0.439	
	21	387.7	0.361	0.435	
He	22	387.7	0.352	0.427	0.428
	12	387.3	0.348	0.429	
	12	386.2	0.336	0.426	
	22	384.1	0.308	0.422	
	22	394.8	0.456	0.437	
HCl	14	394.1	0.489	0.474	0.464
	19	393.1	0.460	0.467	
	18	394.1	0.465	0.451	
He	21	394.2	0.459	0.447	0.433
	9	393.3	0.418	0.418	
SF_6	22	395.6	0.488	0.453	0.444
	12	396.1	0.486	0.435	
$N_2 + NH_3$ (15:1)	17	397.3	0.459	0.367	0.368
	17	397.3	0.421	0.369	
NH_3	16	397.3	0.455	0.398	0.421
	15	397.3	0.507	0.444	
N_2	27	396.9	0.490	0.435	0.423
	27	397.3	0.468	0.410	

The results obtained, in chronological order, are given in Table I. The last column gives the pressure of zinc chloride corrected to a standard temperature. With N_2, He, and SF_6 the results were the same, within experimental error. No measurements by other investigators are available in this temperature range; however, the present data for those gases are within 10% of the value (0.48 mm.) extrapolated from the transpiration data of ref. 4. The results for HCl seemed to be higher than those for the inert gases, which may indicate a small percentage of gaseous $ZnCl_2$–HCl complex; however, it may have been the result of a small, systematic error in handling the HCl relative to the other gases, or an impurity in the HCl.

When the first experiments with NH_3 were analyzed, the weight of material transported was about twice that expected for an inert gas. This apparent evidence in favor of a gaseous complex molecule was found to be due to the transport of NH_4Cl (formed by ammonolysis of $ZnCl_2$) together with the $ZnCl_2$. Two distinct bands of condensate were found in the sample collector. Analysis of four samples of the one that condensed at lower temperatures gave chloride contents ranging from 65.5 to 66.5%. This was concluded to be NH_4Cl (theoretical Cl 66.3%). Chloride analysis of the other band was used to determine the amount of $ZnCl_2$ present. (The amount of Cl in this band was about 92% of that expected for $ZnCl_2$. It is believed that some NH_3 crystallized with the $ZnCl_2$.) When the partial pressures of $ZnCl_2$ in the NH_3-containing gases were calculated from the amounts of $ZnCl_2$ in the condensate, the results shown in Table

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[1] This work was made possible by the support of the Research Division of the U. S. Atomic Energy Commission under contract No. AT(04-3)-106.

[2] For reference see, for example, P. Pascal, "Nouveau Traité de Chimie Minérale," Vol. V, Masson, Paris, 1962, p. 151.

[3] F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958, p. 50.

[4] F. J. Keneshea and D. Cubicciotti, *J. Chem. Phys.*, **40**, 191 (1964).

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

By Richard S. Vinal and L. T. Reynolds

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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 20×10^{-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).