unable to account for the considerable difference in results, but, because our measurements were made with several samples prepared in different ways, we adopt our $\Delta H° = -8.4$ kcal for calculations involving (1).

Combination of our $\Delta H°$ for reaction 1 with $\Delta H_f° = -370.6$ kcal/mole for V_2O_5 from Mah and Kelley[4] and $\Delta H_f°$ for H_2O from NBS Circular 500 gives $\Delta H_f° = -155.3$ kcal/mole for VO_2^+(aq).

Latimer estimated $\Delta G° \cong 2.5$ kcal for reaction 1 from solubility data. More recently, LaSalle and Cobble[3] have reviewed previous solubility measurements and made their own measurements. It now appears that the best $\Delta G°$ for (1) is 1.9 kcal from the data of LaSalle and Cobble. Combination of this $\Delta G°$ with our $\Delta H°$ leads to $\Delta S° = -34.5$ cal/(deg mole of V_2O_5) for (1). Further combination with appropriate entropies[6] leads to $\bar{S}_2° = -9.9$ cal/deg mole and $\Delta G_f° = -140.3$ kcal/mole for VO_2^+(aq).

We have measured the heat of reaction of VO_2^+(aq) with an excess of aqueous ferrous perchlorate solution. The calorimetric reaction equation is

$$Fe^{2+}(\text{concd aq}) + VO_2^+(aq) + 2H^+(aq) = Fe^{3+}(aq) + VO^{2+}(aq) + H_2O \quad (2)$$

All measurements were made with carefully weighed samples (~0.2 g) of V_2O_5 dissolved in 950 ml of $HClO_4$ of concentrations indicated in Table II. Reactions were carried out with 10–25-ml portions of standardized Fe^{2+} solutions (~0.7 *M*) so that final concentrations of Fe^{3+}(aq) were in the range 0.005–0.015 *M*, while V(IV and V) concentrations were about 0.002 *M*. Separate determination of the heat of dilution of the concentrated Fe^{2+} solution as in eq 3 below permitted calculation of the desired ΔH for reaction 4 below, with results given in Table II.

TABLE II

HEATS OF REDUCTION OF VO_2^+ WITH Fe^{2+}(aq)

$[H^+]$, *M*	Moles of $VO_2^+ \times 10^3$	Moles of $Fe^{2+} \times 10^3$	$-Q_2$, cal	$-Q_3$, cal	$-\Delta H_4$, kcal/mole
0.1	1.921	6.75	39.5	1.9	19.6
0.1	1.974	16.88	44.1	5.3	19.7
0.3	1.877	6.23	37.0	1.0	19.2
0.3	2.201	6.23	43.5	1.1	19.3
0.3	2.134	6.75	46.2	4.1	19.7
0.6	2.396	7.58	48.8	2.0	19.5
0.6	2.193	6.75	49.4	6.7	19.5

$$Fe^{2+}(\text{concd}) = Fe^{2+}(aq) \quad (3)$$

$$Fe^{2+}(aq) + VO_2^+(aq) + 2H^+(aq) = Fe^{3+}(aq) + VO^{2+}(aq) + H_2O \quad (4)$$

In eq 2–4 we have used the abbreviation (aq) to indicate that the preceding species are present at low concentrations within the ranges given above. Since all reacting species except H^+ were present at concentrations less than 0.02 *M*, reasonably accurate estimates of heats of dilution lead to $\Delta H° = -19.7$ kcal/mole for (4). Combination of this $\Delta H°$ with our $\Delta H_f°$ for VO_2^+(aq) and other $\Delta H_f°$ values from NBS Circular 500 leads to $\Delta H_f° = -116.3$ kcal/mole for VO^{2+}(aq).

We have also measured the heat of reaction of V_2O_5 (c) with an excess of Fe^{2+}(aq) in $HClO_4$ as represented by

$$V_2O_5(c) + 2Fe^{2+}(aq) + 6H^+(aq) = 2VO^{2+}(aq) + 2Fe^{3+}(aq) + 3H_2O \quad (5)$$

Because of the slowness of the reaction, the best we can report is that $\Delta H_5° = -47 \pm 1$ kcal/mole of V_2O_5. This value is consistent with our earlier results but is not precise enough to warrant further calculations.

Combination of the previously quoted $\Delta G_f°$ for VO_2^+(aq) with the standard potential[2] for the VO^{2+}–VO_2^+ half-reaction leads to $\Delta G_f° = -106.7$ kcal/mole for VO^{2+}(aq). Combination of this $\Delta G_f°$ with $\Delta H_f° = -116.3$ kcal/mole and entropy data[6] leads to $\bar{S}_2° = -32$ cal/deg mole for VO^{2+}(aq).

The VO^{2+}–VO_2^+ potential has been determined at two temperatures,[2] which permits calculation of $\Delta H_f°$ and $\bar{S}_2°$ for VO^{2+}(aq) by combination with the corresponding values for VO_2^+(aq). The results are in reasonable agreement with our values but are much less certain because of the notorious uncertainties associated with deriving slopes from lines based on only two points a few degrees apart. Another approximate approach to these values is by means of the temperature dependence of the equilibrium reduction of VO_2^+ to VO^{2+} by Fe^{2+} (ref 7). Although the relevant equilibrium quotients are for solutions of high ionic strength, we have estimated the corrections that permit calculation of heats and entropies in reasonable agreement with our results.

We judge the values summarized in Table III to be the best that are presently available for VO_2^+(aq) and VO^{2+}(aq).

TABLE III

SUMMARY OF THERMODYNAMIC DATA

	$\Delta G_f°$, kcal/mole	$\Delta H_f°$, kcal/mole	$\bar{S}_2°$, cal/deg mole
VO_2^+(aq)	−140.3	−155.3	−9.9
VO^{2+}(aq)	−106.7	−116.3	−32

Acknowledgment.—We thank the National Science Foundation for support of this research.

[6] K. K. Kelley and E. G. King, U. S. Department of the Interior, Bureau of Mines, Bulletin, No. 592, U. S. Government Printing Office, Washington, D. C., 1961.

[7] W. C. E. Higginson and A. G. Sykes, *J. Chem. Soc.*, 2841 (1962).

CONTRIBUTION FROM REACTION MOTORS DIVISION,
THIOKOL CHEMICAL CORPORATION, DENVILLE, NEW JERSEY

The Chemistry of Alane. XII.[1] The Lithium Tetrahydroalanate–Triethylamine Complex

BY ROBERT EHRLICH[2] AND GEORGE RICE

Received January 10, 1966

In a recent publication by Peters,[3] the reaction of lithium tetrahydroalanate, $LiAlH_4$, with trimethyl-

[1] Paper XI: R. Ehrlich, A. R. Young, II, G. Rice, J. Dvorak, P. Shapiro, and H. F. Smith, *J. Am. Chem. Soc.*, **88**, 858 (1966).

[2] Propellants Laboratory, Feltman Research Laboratories, Picatinny Arsenal, Dover, N. J. Requests for reprints should be sent to A. Marcellis, Reaction Motors Division, Thiokol Chemical Corp., Denville, N J.

[3] F. M. Peters, *Can. J. Chem.*, **42**, 1755 (1964).

amine in diethyl ether was described to yield bis(trimethylamine) alane, $[(CH_3)_3N]_2\cdot AlH_3$, rather than the $(CH_3)_3N$–$LiAlH_4$ complex reported by Wiberg.[4] We wish to report the preparation of the triethylamine complex of $LiAlH_4$, a compound which possesses some remarkable properties. The complex is obtained readily by the addition of anhydrous triethylamine to a suspension of recrystallized $LiAlH_4$ in benzene and evaporation of the benzene filtrate. It is a white, crystalline solid which decomposes without melting above 150°.

Experimental Section

The crude $LiAlH_4$ was purified by solution in diethyl ether and isolation of the soluble portion. The white solid was heated at 45° *in vacuo* to remove the complexed ether. The solid obtained in this manner was better than 98% $LiAlH_4$ based on quantitative hydrolysis. CP triethylamine was dried and stored over LiH, and thiophene-free benzene was dried and stored over $LiAlH_4$. Sodium tetrahydroalanate, $NaAlH_4$, was obtained as a sample from Ethyl Corp. and a benzene solution of $(C_2H_5)_3N\cdot AlH_3$ was prepared as described earlier.[5] All reactions and filtrations were carried out in a nitrogen-atmosphere drybox. Quantitative hydrolyses were performed on a Toepler pump vacuum system.

Preparation of $LiAlH_4\cdot N(C_2H_5)_3$.—To a suspension of 0.10 mole of $LiAlH_4$ in 200 ml of benzene was added 0.10 mole of $(C_2H_5)_3N$. The mixture was stirred 6 hr at ambient temperature, the insoluble material was removed by filtration, and the benzene filtrate was freeze dried leaving 4.43 g (32% of theory) of white solid. The complex did not melt but decomposed above 150°. It ignited when dropped into water or exposed to water vapor. The X-ray diffraction pattern (Table I) was unknown and showed that no $LiAlH_4$ was present.

TABLE I

X-RAY DIFFRACTION PATTERN OF $LiAlH_4\cdot N(C_2H_5)_3$

d, A	*I*/*I*₀	*d*, A	*I*/*I*₀	*d*, A	*I*/*I*₀
8.69	5	3.73	2	2.61	1
6.47	5	3.61	60	2.411	2
6.02	100	3.51	10	2.319	1
5.41	40	3.41	10	2.262	7
5.13	60	3.24	5	2.117	2
4.79	3	3.11	1	2.059	2
4.58	5	2.92	1	1.983	2
4.21	100	2.80	4	1.874	1
4.00	2	2.70	3	1.806	1

Anal. Calcd for $LiAlH_4\cdot N(C_2H_5)_3$: Li, 4.12; Al, 19.44; active H, 2.87; $(C_2H_5)_3N/Al$, 1.0. Found: Li, 4.52; Al, 19.69; active H, 3.00; $(C_2H_5)_3N/Al$, 0.9.

In 2 hr at 148–160° in a Toepler pump vacuum, decomposition was 51.3%, based on total active hydrogen content. The gaseous products, identified by mass spectrometry, consisted of a mixture of hydrogen and triethylamine.

It was not possible to obtain meaningful molecular weight values because the solid complex was only partially soluble in benzene after isolation.

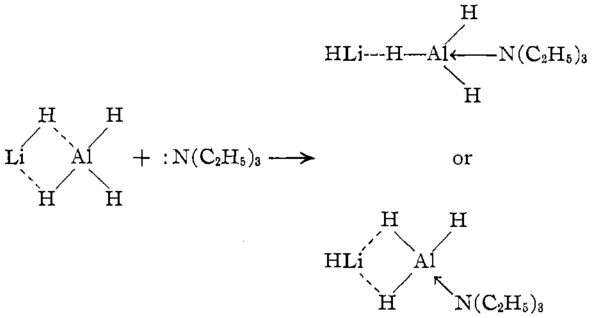
Reaction of LiH and $(C_2H_5)_3N\cdot AlH_3$.—Approximately 1.0 g of LiH was added to 100 ml of a 2 *M* benzene solution of $(C_2H_5)_3N\cdot AlH_3$. The mixture was stirred 48 hr at ambient temperature; then the insoluble residue (1.2 g) was filtered, washed with benzene, and dried *in vacuo* at room temperature for 4 hr. It was identified as $LiAlH_4$ by its infrared spectrum and X-ray diffraction pattern.

The benzene filtrate was freeze dried to give 11.2 g of $LiAlH_4\cdot N(C_2H_5)_3$, identified by comparison to an authentic sample.

Attempted Preparation of $NaAlH_4\cdot N(C_2H_5)_3$.—A suspension of 1.0 g of $NaAlH_4$ in 100 ml of a benzene solution containing 10 g of $(C_2H_5)_3N$ was stirred at room temperature for 15 days. The insoluble portion was shown to be unreacted $NaAlH_4$ while the benzene filtrate contained only $(C_2H_5)_3N$.

Discussion

The most remarkable property of the complex is its infrared spectrum which, both as a KBr pellet and as a solution in benzene, is almost identical with that of triethylamine alane, $(C_2H_5)_3N\cdot AlH_3$. The difference between these two hydrides is especially marked since the latter is a liquid and decomposes above 50° under vacuum. The absence of any absorptions that could be attributed to the AlH_4 grouping indicates that the aluminum is tetracoordinate rather than pentacoordinate. This conclusion also results from the fact that the aluminum in $(C_2H_5)_3N\cdot AlH_3$ is tetracoordinate and that it cannot be converted to a pentacoordinated atom.[6] This inability to form a pentacoordinated aluminum must result in at least a partial displacement of the LiH grouping from the alane coordination sphere, possibly as shown in (1). Then, since LiH absorbs continuously below 2500 cm⁻¹, the only effect of this absorption on the spectrum of triethylamine alane would be a uniform lowering of the base line.



(1)

The implication of the infrared spectroscopic data is that $LiAlH_4\cdot N(C_2H_5)_3$ is actually a complex of $(C_2H_5)_3N\cdot AlH_3$ with LiH rather than a complex of $(C_2H_5)_3N$ with $LiAlH_4$ and should be written as $LiH\cdot AlH_3\cdot N(C_2H_5)_3$. This is also suggested by the formation of $LiH\cdot AlH_3\cdot N(C_2H_5)_3$ from LiH and $(C_2H_5)_3N\cdot AlH_3$ in benzene.[7] In effect then, the $(C_2H_5)_3N\cdot AlH_3$ has become a carrier, or solubilizing agent, for LiH. Substantiation of this has been obtained in the isolation of lithium hexahydroalanate, Li_3AlH_6, from the reaction of $LiAlH_4\cdot N(C_2H_5)_3$ and $LiAlH_4$ and from the interaction of $LiAlH_4\cdot N(C_2H_5)_3$ with diethyl ether.[1] In either case the LiH necessary for the addition to $LiAlH_4$ to give Li_3AlH_6 must have come from the complex.

---

(4) E. Wiberg, H. Nöth, and R. Usón, *Z. Naturforsch.*, **11b**, 486 (1956).

(5) R. Ehrlich, A. R. Young, II, B. M. Lichstein, and D. D. Perry, *Inorg. Chem.*, **2**, 650 (1963).

(6) This has been demonstrated by the inability to form a bis adduct with excess $(C_2H_5)_3N$ and by the failure to show a shift in the Al–H absorption to the lower frequency of a pentacoordinated alane in its infrared spectrum in tetrahydrofuran solution: E. Wiberg and H. Nöth, *Z. Naturforsch.*, **10b**, 237 (1955); J. K. Ruff and M. F. Hawthorne, *J. Am. Chem. Soc.*, **82**, 2141 (1960); **83**, 535 (1961); and unpublished observations in our laboratory.

(7) A similar reaction between LiH and $(CH_3)_3N\cdot AlH_3$ in diethyl ether has been reported to give only $LiAlH_4$: J. K. Ruff and M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 535 (1961).

That the LiH unit is attached to AlH_3 and not to $(C_2H_5)_3N$ is demonstrated by the ability of $LiH \cdot AlH_3 \cdot N(C_2H_5)_3$ to act as if the $LiH \cdot AlH_3$ were a molecular entity in its reaction with commercial grade LiH in benzene to give Li_3AlH_6.[1] Under the same condition $LiAlH_4$ will not react with LiH.

When triethylamine was added to a diethyl ether solution of $LiAlH_4$, we obtained results similar to those reported by Peters[3] except that the soluble portion was $LiH \cdot AlH_3 \cdot N(C_2H_5)_3$ rather than $(C_2H_5)_3N \cdot AlH_3$. An attempt to prepare $NaAlH_4 \cdot N(C_2H_5)_3$ in benzene was unsuccessful.

Acknowledgment.—We wish to acknowledge the assistance of Raymond N. Storey in the determination and interpretation of the infrared spectra.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CORNELL UNIVERSITY, ITHACA, NEW YORK

Inner- and Outer-Sphere Complex Formation in Aqueous Solutions of Nickel(II)–Methyl Phosphate[1]

BY HANS BRINTZINGER AND GORDON G. HAMMES

Received January 24, 1966

The relative amounts of outer-sphere ion pairs (ML_o) and inner-sphere coordination compounds (ML_i) present in solutions of metal complexes are difficult to assess experimentally. A knowledge of the relative amounts is of particular interest in biological systems involving mono- and diphosphate esters. We present here a direct measurement of the ratio $(ML_o)/(ML_i)$ for Ni^{2+} complexes of methyl phosphate (MP) by use of the temperature-jump method. Methyl phosphate was selected for study because its metal complexes are considerably more soluble than those of most monophosphate esters (*e.g.*, adenosine 5′-monophosphate). Some of the related kinetic constants also have been obtained.

Experimental Section

All solutions were 0.1 *M* in NaCl and 2×10^{-5} *M* in chlorophenol red at pH 6.8. The $NiCl_2$ used was standard reagent grade; the methyl phosphate was prepared as previously described.[2] The temperature-jump apparatus and experimental procedure have been described in detail elsewhere.[3,4] The change in pH resulting from the shift in concentrations of the reactants was followed by observing the absorbancy changes at 573 mμ and the final temperature was 25°.

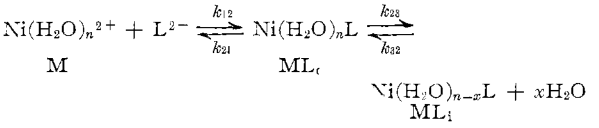
Results and Treatment of Data

Relaxation effects were observed only when the total nickel and ligand concentrations were in the range 0.005 to 0.1 *M*. The relaxation times were evaluated from a plot of the logarithm of the signal amplitude *vs.* time; the straight line obtained indicates a single relaxation process is being observed. The relaxation times obtained and the total metal and ligand concentrations used are summarized in Table I.

TABLE I
RELAXATION TIMES AND TOTAL METAL AND LIGAND CONCENTRATIONS

τ, μsec	$10^2\Sigma Ni$, *M*	$10^2\Sigma MP$, *M*
85	10.0	10.0
95	4.00	4.00
100	1.60	1.60
120	0.64	0.64

The generally accepted mechanism of complex formation between Ni^{2+} and a ligand L^{2-} is (*cf.* ref 3 and 5)



$$\underset{M}{Ni(H_2O)_n{}^{2+}} + L^{2-} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \underset{ML_o}{Ni(H_2O)_nL} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \underset{ML_i}{Ni(H_2O)_{n-x}L} + xH_2O \quad (1)$$

(Methyl phosphate, in the pH range under consideration, is either a mono- or divalent anion, but only the divalent species is assumed to react with Ni^{2+}.) For all of the Ni complexes studied thus far, with the temperature-jump method, the concentration of ML_o has been assumed to be very small compared to ML_i and the formation of the outer-sphere complex has been assumed to be rapid compared to the rate of expulsion of water molecules from the inner coordination sphere of the metal ion. In this case the relaxation time is given by[3]

$$1/\tau = K_{12}k_{23}[(M)/(1 + \alpha) + (L)] + k_{32} \quad (2)$$

where $K_{12} = k_{12}/k_{21}$ and α is a known factor which takes into account the rapid protolytic reactions also occurring. The concentration dependence of the relaxation times observed in the present cases is not consistent with eq 2. However, if we assume that the concentration of ML_0 is not negligible, but that ion-pair formation and adjustment of protolytic equilibria are still rapid compared to dissociation of the water molecules, the slow relaxation time for eq 1 is (a general procedure for calculating relaxation times is given in ref 6)

$$1/\tau = k_{32} + \cfrac{k_{23}}{1 + \cfrac{1 + \alpha'}{K_{12}(L) + \alpha' K_{12}[(M) + (L)]}}$$

with (3)

$$\alpha' = \cfrac{(L)/(H)}{1 + \cfrac{K_I(In)}{1 + K_I(H)}} + \frac{1}{K_A(H)}$$

where K_I is the acid association constant of the indicator ($10^{6.2}$ M^{-1} for chlorophenol red), K_A is that of the

---

[1] This work was supported by grants from the National Institutes of Health (GM13292) and the National Science Foundation (GP4623).

[2] H. Brintzinger, *Helv. Chim. Acta*, **48**, 47 (1965).

[3] G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962).

[4] G. G. Hammes and P. Fasella, *ibid.*, **84**, 4644 (1962).

[5] M. Eigen and R. G. Wilkins in Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1966.

[6] M. Eigen and L. de Maeyer in "Technique of Organic Chemistry," Vol. 8, Part 2, L. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 895.