an increasing discrepancy between the calculated and measured values with increasing mass of the group 3A metal. These discrepancies can be explained by changed coupling of the MOH stretching and bending modes of a nonlinear molecule.

The photolytic reaction of diatomic group 3A molecules with water occurs at longer wavelengths than for the atom and produces a group of absorption peaks in the 850–1050-cm⁻¹ region. Deuterium isotopic shifts indicate that the vibrational mode is primarily a hydrogen motion, although there is a slight oxygen-18 dependence. We have suggested that the mode may be best explained as an asymmetric mode of a bridging hydrogen. The location of modes due to a bridging hydrogen should be ~1000 and ~900 cm⁻¹ for gallium and indium, respectively, if one assumes a similar ratio of frequencies as that found for the asymmetric bridging and terminal stretching modes of diborane. One also expects the hydroxyl group to be bridging. It is possible to view the HM₂OH molecule as a mixed dimer of monovalent MH and MOH species which suggests that dimers of MH and MOH would also exist as bridging structures. Prolonged photolysis at shorter wavelengths converts the HM₂OH species to the known high-temperature M₂O species.

The dihydroxyaluminum hydride has been identified and presumably results from further reaction of the HAlOH(H₂O) species. We did not observe a similar dihydroxy species for gallium and indium, which may suggest that the higher oxidation state HM(OH)₂ is unstable with respect to the MOH(H₂O) species. In fact, the unassigned peaks listed in Table III for indium could be due to InOH(H₂O).

The inability of thallium to react was discussed earlier. However, after prolonged photolysis, we do observe a peak labeled

"h". We have suggested that the peak may be assigned to TlOH or TlOH(H₂O). Although the reaction is endothermic and the excited state HTl*OH is expected to revert to Tl···OH₂, some probability may exist for breaking of the H–Tl bond and subsequent diffusion of the hydrogen into the matrix, thereby stabilizing the TlOH species. The alternative assignment as TlOH(H₂O) formation could result from stabilization of TlOH by interaction with water. It is interesting to note that a dithallium product species does readily form, which suggests that a bridging structure has stabilized the hydrogen and hydroxyl bonds sufficiently to favor the photolysis product over the adduct.

The reaction chemistry of group 3A metals with water may be summarized as follows:

$$M + H_2O \rightarrow M\cdots OH_2 \xrightarrow{h\nu_1} HMOH \rightarrow H + MOH$$
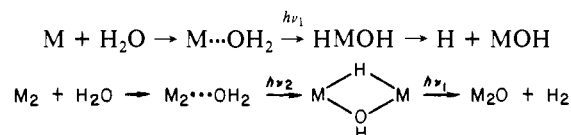
The exception is Al, which spontaneously reacts with water as follows:
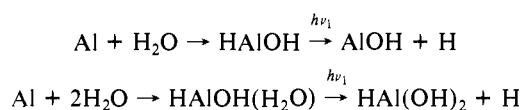
$$Al + H_2O \rightarrow HAlOH \xrightarrow{h\nu_1} AlOH + H$$

$$Al + 2H_2O \rightarrow HAlOH(H_2O) \xrightarrow{h\nu_1} HAl(OH)_2 + H$$

A Nuclear Magnetic Resonance Study of *tert*-Butoxyaluminates

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Abstract: ¹H, ⁷Li, ¹³C, and ²⁷Al NMR studies of lithium *tert*-butoxyaluminates have been carried out in THF solution. While the ⁷Li study was not particularly informative, the ¹H, ¹³C, and ²⁷Al studies clearly show that Li(*t*-BuO)AlH₃ does not exist in THF solution in large enough concentration to be detected. It was found that the equilibrium $3Li(t\text{-BuO})_2AlH_2 \rightleftharpoons 2Li(t\text{-BuO})_3AlH + LiAlH_4$ is present with $K_{eq} = 2.2 \times 10^{-2}$.

Introduction

Since the discovery of lithium aluminum hydride more than 30 years ago, considerable work has been devoted to modify its reactivity by the addition of alcohols to produce lithium alkoxyaluminum hydrides.[1] Because of the apparent stability of lithium *tert*-butoxyaluminum hydrides in tetrahydrofuran (THF) solution, and the selectivity of reduction by Li(*t*-BuO)₃AlH, *tert*-butyl alcohol has received the most attention as a modifying alcohol for LiAlH₄.[1b–d]

Two reports have appeared in the literature concerning the nature of the solute species for lithium *tert*-butoxyaluminum hydride. Kader[2] described a ¹H NMR study in ether–THF solvent in which he interpreted the proton resonances of his solutions as due to three species: Li(*t*-BuO)AlH₃, Li(*t*-BuO)₂AlH₂, and Li(*t*-BuO)₃AlH. Ashby[3] reported ebullioscopic and conductance

measurements on THF solutions prepared by adding 1 or 3 mol of *tert*-butyl alcohol per mol of LiAlH₄. Ashby concluded that in THF Li(*t*-BuO)₃AlH is monomeric over a concentration range of 0.05–0.5 m (association (*i*) ~ 1), and Li(*t*-BuO)AlH₃ is associated (*i* = 1.3 at 0.4 m). He did not report data for Li(*t*-BuO)₂AlH₂.

The new experiments described below involve ¹H, ⁷Li, ¹³C, and ²⁷Al NMR studies of 0.4 M solutions of LiAlH₄ in THF containing molar ratios of *tert*-butyl alcohol to LiAlH₄ of from 0.5 to 3.0. The results show that from molar ratio of 0.5 to 2.0 the predominant lithium *tert*-butoxyaluminate is Li(*t*-BuO)₂AlH₂. Evidence for Li(*t*-BuO)AlH₃ could not be found in THF even at molar ratios as low as 0.5.

Experimental Section

The LiAlH₄ solutions were prepared by stirring LiAlH₄ with anhydrous THF containing 1% v/w benzene-*d₆* under nitrogen and filtering. The chemical shifts for ²⁷Al and ⁷Li in LiAlH₄ were measured by sus-

(1) (a) For a review see: Malek, J.; Cerng, M. *Synthesis* **1972**, 217. (b) Brown, H. C.; McFarlin, R. F. *J. Am. Chem. Soc.* **1958**, *80*, 5372. (c) Haubenstock, H.; Eliel, E. *Ibid.* **1962**, *84*, 2363. (d) Brown, H. C.; Shoaf, C. J. *Ibid.* **1964**, *86*, 1079.

(2) Kader, M. *Tetrahedron Lett.* **1969**, 2301.

(3) Ashby, E. C.; Dobbs, F. R.; Hopkins, H. P., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 3158.
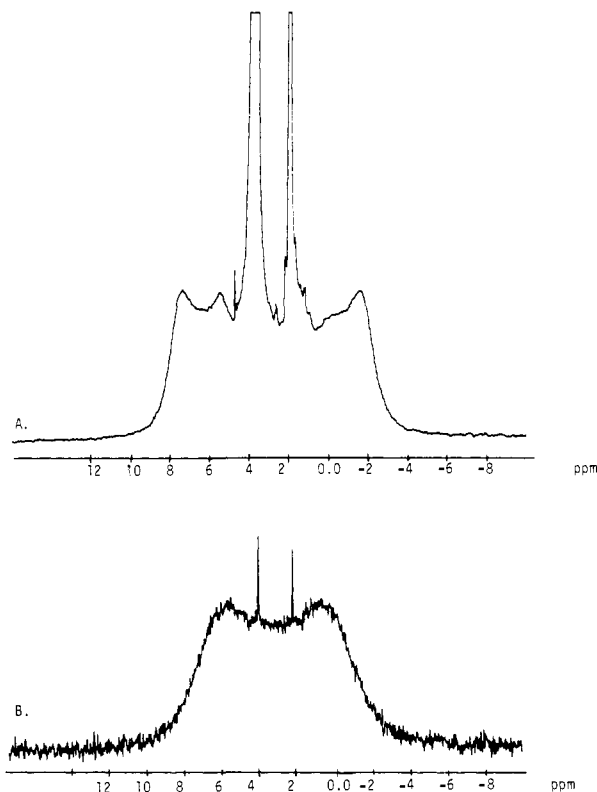
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Horne

Figure 1. (A) ^1H NMR spectrum of $LiAlH_4$ in 98% THF-d_8. (B) ^2H NMR spectrum of $LiAlD_4$ in THF.

pending a sealed capillary containing a solution which was 0.5 M each in aluminum sulfate and lithium sulfate. The concentration of the $LiAlH_4$ solutions was determined prior to each run by measuring the hydrogen evolved when an aliquot was quenched in 1:1 THF–1 M H_2SO_4.[4] *tert*-Butyl alcohol was added either neat or as a 50% solution in THF to an ice-cold stirred aliquot of the $LiAlH_4$ solution. The evolution of hydrogen was measured as the *tert*-butyl alcohol was added. In each case 1 mol of hydrogen was observed for each mol of *tert*-butyl alcohol added. NMR spectra (JEOL FX·90Q spectrometer) were obtained using 10-mm tubes at –5 °C in THF with 1% benzene-d_6 added for internal lock. The ^1H, ^7Li, ^{13}C, and ^{27}Al spectra were recorded on the same sample for each *tert*-butyl alcohol/$LiAlH_4$ ratio using a broad band probe module.

Results

The ^{27}Al spectrum of $LiAlH_4$ in several ether solvents was reported by Heřmánek.[5a] It was found that in ethyl ether the spectrum consisted of a broad singlet due to an unsymmetrical aluminum environment caused by lithium coordination to the tetrahydroaluminate ion. An unsymmetrical aluminum environment causes angular dependence of the electric field gradients around the quadrupolar ^{27}Al nucleus and therefore a broad signal. In stronger ether solvents like THF or dimethoxyethane the spectrum was resolved into a proton-coupled quintet. In these solvents lithium is better solvated leaving the tetrahydroaluminate ion in an environment of cubic symmetry.

Our ^7Li data support this view. The ^7Li spectrum for $LiAlH_4$ in THF consists of a sharp singlet (width 1/2-height = 2 Hz) 0.64 ppm upfield from $^7Li(H_2O)_6{}^+$. The chemical shift and the line width do not change as the *tert*-butyl alcohol/$LiAlH_4$ ratio is increased. If the lithium ion is separated from the aluminate ion, then one should expect the ^7Li chemical shift to remain the same for $LiAlH_4$ and $Li(t\text{-}BuO)_3AlH$. Therefore, the lithium ion is solvent separated from the aluminate ion in THF solvent.
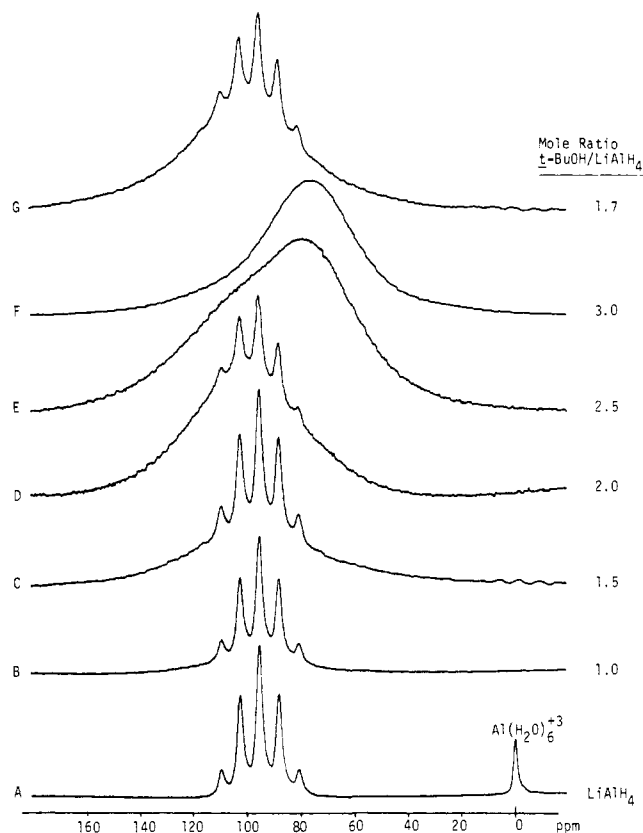
(4) Brown, H. C. "Organic Synthesis via Boranes"; Wiley: New York, 1975; p 241.

(5) (a) Hermanek, S.; Kriz, O.; Plesek, J.; Hanslik, T. *Chem. Ind. (London)* **1975**, 42. (b) Santini, R. E.; Grutzner, J. B. *J. Magn. Reson.* **1976**, *22*, 155.

(6) Amplitude of the signals is scaled by the instrument for each run. Therefore, the amplitudes cannot be related to relative concentrations.

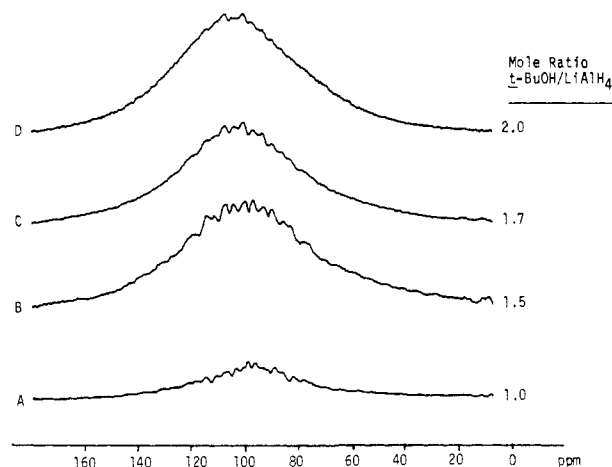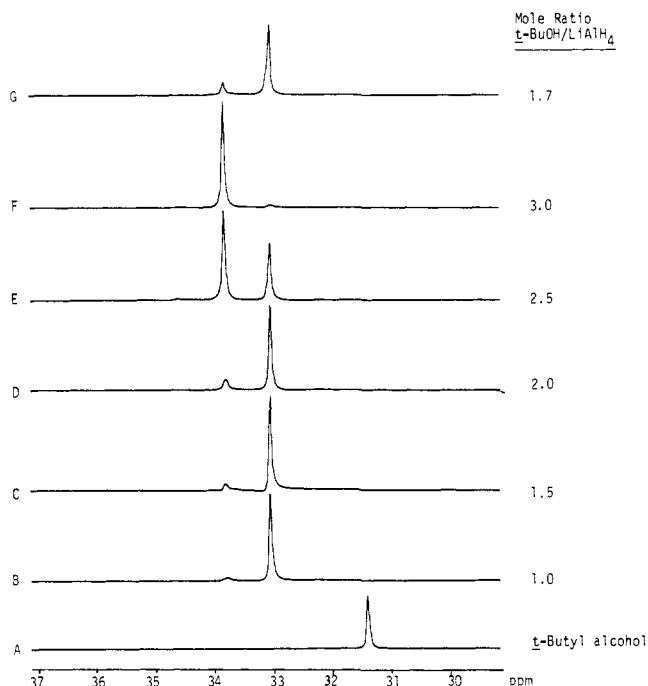**Figure 2.** The 23.30-MHz ^{27}Al spectra in THF[6].

Figure 3. The ^{27}Al residual spectra after the substraction of $LiAlH_4$ quintet.[6]

Table I. Calculated Equilibrium Constants for Several *tert*-Butyl Alcohol/$LiAlH_4$ Molar Ratios

t-BuOH/$LiAlH_4$	R_C	R_{Al}	K_{eq}
1.0	0.11	1.05	3.3×10^{-2}
1.5	0.17	0.27	2.2×10^{-2}
1.7	0.22	0.12	1.7×10^{-2}
2.0	0.25	0.092	1.8×10^{-2}

Only sketchy data are available for the proton spectrum of $LiAlH_4$.[2] Internuclear double resonance experiments indicated that the chemical shift for the hydride protons was near the THF protons. This was confirmed by direct observation in THF-d_8 of $LiAlH_4$ and of $LiAlD_4$ by ^2H magnetic resonance in THF (Figure 1). The broad signals (width at 1/2-height = 10 ppm) are due to coupling to aluminum ($I = 5/2$, $J = 172$ Hz for proton). The signals for the hydride protons in *tert*-butoxyaluminates should be even broader owing to the aluminum quadrupole in an un-

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Figure 4. The 22.50-MHz ^{13}C spectra in THF. Methyl carbons of *tert*-butyl alcohol.[6]

symmetrical environment and thus much more difficult to observe.

Figure 2 displays the ^{27}Al spectra taken at 23.30 MHz for several *tert*-butyl alcohol/LiAlH$_4$ molar ratios. The ^{27}Al–^{1}H coupling observed for LiAlH$_4$ of 173 Hz is consistent with the previously reported values of 172[5a] and 175 Hz[5b]. As the *tert*-butyl alcohol/LiAlH$_4$ ratio approaches 2 a new quadrupole-broadened singlet grows in at the expense of the LiAlH$_4$ quintet. This can be seen in Table I and in Figure 3; R_{Al} is the ratio of the area of the LiAlH$_4$ quintet to the broadened singlet. As the ratio increases from 2 to 3 a new quadrupole-broadened singlet appears –21.9 ppm from the LiAlH$_4$ quintet.

Figure 4 displays the ^{13}C spectra taken at 22.50 MHz of the methyl carbons of the *tert*-butoxy groups. Up to a molar ratio of 2.0, one finds one major signal 1.63 ppm from *tert*-butyl alcohol and a second smaller signal at 2.43 ppm. From a molar ratio of 2 to 3 the 2.43-ppm signal grows until it is the major peak at a molar ratio of 3.

Figure 5 displays the ^{1}H of the *tert*-butoxy groups taken at 89.56 MHz. Up to a molar ratio of 2 one finds one signal 0.027 ppm from *tert*-butyl alcohol. From a molar ratio of 2 to 3 a second signal grows in at 0.038 ppm until it is the major peak at a molar ratio of 3.

Brown[1b,d] reported that lithium tri-*tert*-butoxyaluminate (Li-(*t*-BuO)$_3$AlH) reacts slowly at 80 °C in dimethoxyethane with *tert*-butyl alcohol to give Li(*t*-BuO)$_4$Al, which was found to be insoluble in ether solvents. We have found that Li(*t*-BuO)$_4$Al may be prepared by refluxing Li(*t*-BuO)$_3$AlH with a 10% molar excess of *tert*-butyl alcohol in THF overnight. However, we find Li(*t*-BuO)$_4$Al to be soluble in THF, at least in the concentration range in which we are working (0.4 M aluminate). The ^{27}Al NMR of Li(*t*-BuO)$_4$Al consists of a narrow singlet (width at 1/2-height = 257 Hz) –46.7 ppm from the LiAlH$_4$ quintet. The ^{13}C NMR consists of a singlet for the *tert*-butoxy methyl carbons at 2.47 ppm from *tert*-butyl alcohol; the ^{1}H NMR consists of a singlet 1.15 ppm from the *tert*-butyl alcohol methyl singlet.

Discussion

In all of the experiments 1 mol of hydrogen was liberated for each mol of *tert*-butyl alcohol added to the LiAlH$_4$ solution. Therefore, the number of moles of *tert*-butyl alcohol added to the solution should be proportional to the concentration of *tert*-butoxyaluminates in each solution. Thus, if there are no competing reactions, as one adds *tert*-butyl alcohol to a LiAlH$_4$ solution the concentration of Li(*t*-BuO)AlH$_3$ should increase and the con-
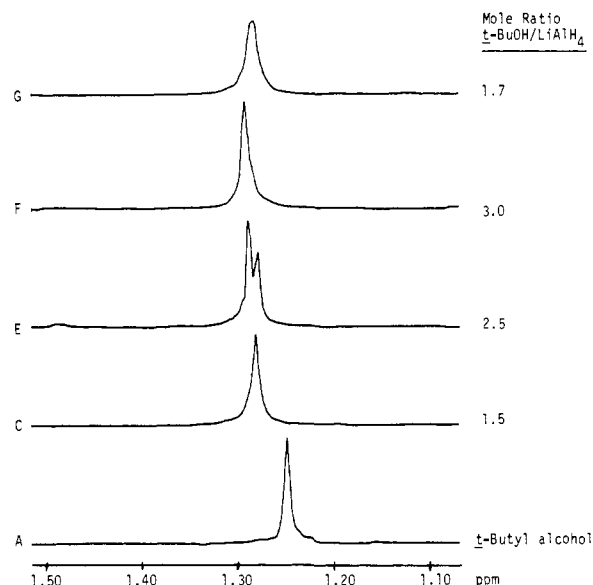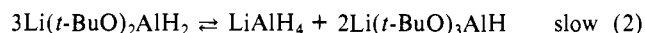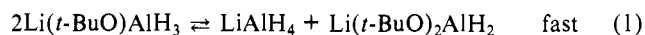

Figure 5. The 89.56-MHz proton spectra in THF. Methyl protons of *tert*-butyl alcohol.[6]

centration of LiAlH$_4$ should decrease until a molar ratio of *tert*-butyl alcohol/LiAlH$_4$ equal to 1 is reached. As one continues to add *tert*-butyl alcohol from a molar ratio of 1 to 2 the concentration of Li(*t*-BuO)$_2$AlH$_2$ should increase at the expense of Li(*t*-BuO)AlH$_3$, and similarly from a molar ratio of 2 to 3 the concentration of Li(*t*-BuO)$_3$AlH should increase at the expense of Li(*t*-BuO)$_2$AlH$_2$. One should then see resonances in NMR spectra of these solutions for LiAlH$_4$ and Li(*t*-BuO)AlH$_3$ up to a molar ratio of 1; Li(*t*-BuO)AlH$_3$ and Li(*t*-BuO)$_2$AlH$_2$ from a molar ratio of 1 to 2; Li(*t*-BuO)$_2$AlH$_2$ and Li(*t*-BuO)$_3$AlH from a molar ratio of 2 to 3. Except from a molar ratio of 2 to 3 our NMR data does not fit this simple solution system.

The ^{13}C data (Figure 4) may be interpreted in two ways. Either there is only one dominant *tert*-butoxyaluminate species in solution at molar ratios of *tert*-butyl alcohol/LiAlH$_4$ up to 2, or there is a rapid equilibrium between Li(*t*-BuO)AlH$_3$ and Li(*t*-BuO)$_2$AlH$_2$ followed by a slow equilibrium between Li(*t*-BuO)$_2$AlH$_2$ and Li(*t*-BuO)$_3$AlH:

$$2\text{Li}(t\text{-BuO})\text{AlH}_3 \rightleftharpoons \text{LiAlH}_4 + \text{Li}(t\text{-BuO})_2\text{AlH}_2 \qquad \text{fast} \qquad (1)$$

$$3\text{Li}(t\text{-BuO})_2\text{AlH}_2 \rightleftharpoons \text{LiAlH}_4 + 2\text{Li}(t\text{-BuO})_3\text{AlH} \qquad \text{slow} \qquad (2)$$

In either case there should be one dominant resonance for the *tert*-butyl methyl carbons, in one case because there is only one dominant species in solution, and in the other because the resonances expected for Li(*t*-BuO)AlH$_3$ and Li(*t*-BuO)$_2$AlH$_2$ are coalesced into one resonance with chemical shift intermediate between the two. In the ^{27}Al data (Figure 2) one finds the LiAlH$_4$ quintet sitting on top of a quadrupole broadened singlet at molar ratios of *tert*-butyl alcohol/LiAlH$_4$ up to 2. The chemical shift and the line width of this quintet do not change with changing molar ratios. This clearly rules out the presence of a fast equilibrium involving LiAlH$_4$ because such an equilibrium would cause the quintet to be broadened and its chemical shift to change. Thus there must be one dominant *tert*-butoxyaluminate in solution up to a molar ratio of 2 and on the basis of the stoichiometric release of hydrogen along with the changes in the NMR signals upon addition of *tert*-butyl alcohol up to a molar ratio of 2 the dominant species must be Li(*t*-BuO)$_2$AlH$_2$.

One may reasonably assign the ^{13}C singlet at 1.63 ppm from *tert*-butyl alcohol methyl carbons (Figures 4B–G) and the ^{27}Al quadrupole broadened singlet which grows in under the LiAlH$_4$ quintet (Figures 2B–E) to Li(*t*-BuO)$_2$AlH$_2$. The ^{13}C singlet at 2.43 ppm and the ^{27}Al quadrupole broadened singlet –21.9 ppm from the LiAlH$_4$ quintet may reasonably be assigned to Li(*t*-BuO)$_3$AlH.

Since one finds the ^{13}C singlet for Li(*t*-BuO)$_3$AlH even at low molar ratios of *tert*-butyl alcohol/LiAlH$_4$ a reasonable suggestion

is that Li(*t*-BuO)$_2$AlH$_2$, Li(*t*-BuO)$_3$AlH, and LiAlH$_4$ are in slow equilibrium according to eq 2. Confirmation of this suggestion was sought by approaching the equilibrium from the opposite direction. If this equilibrium is present, one should be able to start with a solution of Li(*t*-BuO)$_3$AlH and add LiAlH$_4$ to reestablish the equilibrium. Spectrum G in Figures 2–4 was obtained in just such a manner. To a solution of Li(*t*-BuO)$_3$AlH (spectrum E in Figures 2, 4, and 5) was added a solution of LiAlH$_4$ so that the new molar ratio was 1.7. Note that in the ^{27}Al spectrum (Figure 2) the broad singlet –21.9 ppm from LiAlH$_4$ is gone and that in the ^{13}C spectrum (Figure 4) the singlet for Li(*t*-BuO)$_3$AlH is nearly gone while the singlet for Li(*t*-BuO)$_2$AlH$_2$ has reappeared.

From the ratio of the integrated areas of the methyl singlets in the ^{13}C spectrum one can obtain the ratio R_C:

$$2[\text{Li}(t\text{-BuO})_3\text{AlH}]/3[\text{Li}(t\text{-BuO})_2\text{AlH}_2] = R_C \qquad (3)$$

The ^{27}Al spectra of solutions containing *tert*-butyl alcohol/LiAlH$_4$ molar ratios between 0.5 and 2.0 consist of a broad singlet due to Li(*t*-BuO)$_2$AlH$_2$ and Li(*t*-BuO)$_3$AlH with a quintet from LiAlH$_4$ imposed upon it. Using the instruments computer, one may subtract the LiAlH$_4$ quintet from the spectra to obtain just the broad singlet whose area is proportional to the concentration of Li(*t*-BuO)$_2$AlH$_2$ plus Li(*t*-BuO)$_3$AlH; the resulting broad singlets are shown in Figure 3. In this way one may determine the ratio R_{Al}:

$$\frac{[\text{LiAlH}_4]}{[\text{Li}(t\text{-BuO})_2\text{AlH}_2] + [\text{Li}(t\text{-BuO})_3\text{AlH}]} = R_{Al} \qquad (4)$$

Together, these ratios allow the calculation of the equilibrium constant

$$K_{eq} = \frac{[\text{Li}(t\text{-BuO})_3\text{AlH}]^2[\text{LiAlH}_4]}{[\text{Li}(t\text{-BuO})_2\text{AlH}_2]^3} \qquad (5)$$

Combining eq 3–5 one can obtain

$$K_{eq} = (3/2R_C)^2 R_{Al}(3/2R_C + 1) \qquad (6)$$

The data in Table I indicate an equilibrium constant of 2.2×10^{-2}.

Conclusions

We find that for molar ratios for *tert*-butyl alcohol/LiAlH$_4$ up to 2 the major *tert*-butoxyaluminate in solution is Li(*t*-BuO)$_2$AlH$_2$ and that it is in a slow equilibrium with LiAlH$_4$ and Li(*t*-BuO)$_3$AlH. If Li(*t*-BuO)AlH$_3$ is present, its concentration must be low compared to the Li(*t*-BuO)$_2$AlH$_2$ concentration. Clearly the *tert*-butoxyaluminate system is not as simple a system as some have thought it to be.

Hydrogen-Bonding Interactions Involving Metal-Bound Dioxygen

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Abstract: In this article the equilibrium constant and enthalpy for formation of the dioxygen adduct of the bis(salicyliden-iminato-3-propyl)methylaminocobalt(II) complex (CoSMDPT) are reported in methylene chloride solution (–9.8 kcal mol^{-1}). When small amounts of 2,2,2-trifluoroethanol (TFE) are added, extra stabilization of the dioxygen adduct is found. The measured enthalpy for adduct formation increases to –11.8 kcal mol^{-1}. Infrared frequency shift studies of the O–H stretching vibration indicate that TFE undergoes a hydrogen-bonding interaction with the coordinated dioxygen. An enthalpy-frequency shift, $\Delta\nu$OH, relation provides an estimate of a 6.6 kcal mol^{-1} hydrogen bond strength. This is one of the few instances in which a clear-cut reaction of the coordinated dioxygen is shown. This interaction suggests an explanation for the high oxygen affinities of such systems as cobalt myoglobin and CoTpivPP·MeIm compared to cobalt(II) protoporphyrin IX dimethyl ester.

Introduction

The reversible binding of dioxygen in biological systems and interest in the activation of dioxygen by metal ions in biological as well as commercial processes have led to extensive activity in the area of metal–dioxygen systems.[1–5] Results from this laboratory[2–4] have led to the formulation of the spin-pairing model for dioxygen binding. The metal–dioxygen bonding interaction is viewed as resulting from a pairing up of the spins (bonding) of metal electrons with unpaired electrons in the π^* orbital of dioxygen. An EPR analysis indicates that partial negative charges on the bound O$_2$ of some cobalt complexes vary from 0.1 to 0.8 depending upon the ligands bound to the metal.[3]

Several important questions remain to be answered in the areas of dioxygen binding and activation. The question of dioxygen activation is very intimately connected with the reactivity and nucleophilicity of bound O$_2$. However, very little chemistry involving metal-bound dioxygen has been reported. The 1:1 dioxygen adduct (referred to as a superoxo complex) can react with a second cobalt(II) complex forming a 2:1 adduct (referred to as a μ-peroxo complex).[1b] The cobalt(II)-catalyzed oxidation of phenol has been proposed to involve a mechanism in which phenol hydrogen bonds to the coordinated dioxygen in the course of undergoing a hydrogen-atom abstraction to produce the phenoxy radical.[6] A better appreciation for the factors influencing the reactivity of bound O$_2$ is essential to the understanding of the catalytic activation of this molecule.

A widely held view of the nature of the bound dioxygen consideres it to be a superoxide ion that is bound ionically to the cobalt.[1a,c] The superoxide ion has been shown to be a potent nucleophile.[7] Quantitative information about the basicity or

(1) For a review of early work see (a) F. Basolo, B. M. Hoffman, and J. A. Ibers, *Acc. Chem. Res.*, **8**, 384 (1975), and references cited therein; (b) L. Vaska, *ibid.*, **9**, 175 (1976); (c) J. P. Collman *ibid.*, **10**, 265 (1977); (d) G. McLendon and A. E. Martell, *Coord. Chem. Rev.*, **19**, 1 (1976).

(2) R. S. Drago, T. Beugelsdijk, J. A. Breese, and J. P. Cannady, *J. Am. Chem. Soc.*, **100**, 5374 (1978).

(3) B. S. Tovrog, D. J. Kitko, and R. S. Drago, *J. Am. Chem. Soc.*, **98**, 5144 (1976).

(4) R. S. Drago, *Inorg. Chem.*, **18**, 1408 (1979).

(5) For a theoretical analysis see B. H. Huynh, D. A. Case, and M. Karplus, *J. Am. Chem. Soc.*, **99**, 6103 (1977), and references cited therein.

(6) A. Nishinago, H. Tomita, T. Shimizu, and T. Matsuura in "Fundamental Research in Homogeneous Catalysis", Vol. 2, Y. Ishii and M. Tsutsui, Eds., Plenum Press, New York, 1978, and references cited therein.