dependent pathways remain the more rapid step due to the large thermodynamic driving force of the redox reaction derived from the couple $HMnO_4/HMnO_4^-$ ($E° \approx 1.11$ V).[2b]

Although the form of the rate law provides no detailed information concerning an inner- or outer-sphere mechanism, the aquomolybdenum(V) dimer has been compared in recent studies to aquovanadium(IV).[19,20] Both ions are d^1 systems and are similar in their overall structure as both contain terminal oxo groups. Solid-state structural data show a lengthening of the bond to the trans ligand for various compounds of both ions, and it is thought that the terminal oxo group weakens the bond trans to it.[21] This weakened bond is felt to be responsible for the rapid exchange of the trans ligand with solvent in $Mo_2O_4(NCS)_6^{4-}$.[22] A comparison of the rate constants from the expression $k_2 = k_O + k'_H K_{Mn}[H^+]$ for the reaction of MnO_4^- with the aquo dimer and VO^{2+} shows the dimer is more rapidly oxidized. The sizes of the ratios $k_O(\text{dimer})/k_O(VO^{2+}) \approx 74$ and $k'_H(\text{dimer})/k'_H(VO^{2+}) \approx 10$ appear to suggest a similar mechanism for these ions with MnO_4^-.[23,24]

Sykes has called the $(H_2O)_6Mo_2O_4^{2+}$ ion an outer-sphere reductant from comparison of rate and thermodynamic data from the reaction of $Mo_2O_4^{2+}$ and $Mo_2O_4(EDTA)^{2-}$ with those for the reaction of $IrCl_6^{2-}$ and $Fe(phen)_3^{3+}$, both outer-sphere oxidants.[13] Table IV presents data from the oxidation of $Mo_2O_4^{2+}$ and VO^{2+} by MnO_4^- and several other oxidants. It is interesting to note that, while the values of $\Delta H^{\ddagger}$ for the reactions of MnO_4^- with $Mo_2O_4^{2+}$ and VO^{2+} are similar and not unlike those of the $Mo_2O_4^{2+}/Fe(phen)_3^{2+}$ reaction, the activation entropy, $\Delta S^{\ddagger}$, values differ considerably. It has been shown[2b,3] that $\Delta S^{\ddagger}$ values for a group of outer-sphere reactant/MnO_4^- reactions tend to be much more positive (−5.6 to +36.5 cal/(mol K)) than $\Delta S^{\ddagger}$ for a set of inner-sphere reactants (−13 to −30 cal/(mol K)).[26] An isokinetic plot using $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values from various reductant/MnO_4^- reactions also shows the aquo dimer behaves as an outer-sphere reductant and not an inner-sphere reactant like VO^{2+}.

Since the aquo Mo(V) dimer can be considered a one-electron reductant with MnO_4^-, an $E°$ value was estimated for the reaction $Mo^V_2 \rightarrow Mo^VMo^{VI} + e^-$, from a plot of the rate constants for the unprotonated pathways, log k_O, vs. $E°$(reductant) for a series of MnO_4^-/inorganic ion reactions.[27] The value, −0.53 V, is in reasonable agreement with the one-electron value of −0.52 to −0.56 V estimated by Pope from studies of Mo(V)-substituted "Keggin anions".[11]

Results ($\Delta H^{\ddagger}$, kcal/mol; $\Delta S^{\ddagger}$, cal/(mol K)) from complexation studies of SCN^- with $(H_2O)_6Mo^V_2$ (11.3, −0.3) and VO^{2+} (10.8, −3.7) have been interpreted as indicating substantial involvement of the equatorial position with the incoming ligand.[19] It is likely that the interaction of the permanganate ion with these two ions is similar. We are presently examining this idea.

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Registry No. MnO_4^-, 14333-13-2; $Mo_2O_4^{2+}$, 54429-28-6.

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(18) N. Bailey, A. Carrington, K. A. K. Lott, and M. C. R. Symons, *J. Chem. Soc.*, 290 (1960).

(19) Y. Sasaki, R. S. Taylor, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 396 (1975).

(20) R. K. Murmann, *Inorg. Chim. Acta*, **25**, L43 (1977).

(21) D. L. Kepert, "The Early Transition Metals", Academic Press, London, 1972, p 318, and references within; K. B. Swedo and J. H. Enemark, *J. Chem. Educ.*, **56**, 70 (1979).

(22) S. Wajda and A. Zarzeczny, *Nukleonika*, **19**, 33 (1974); *Chem. Abstr.*, **81**, 69217*r* (1974).

(23) J. P. Birk and S. V. Weaver, *Inorg. Chem.*, **11**, 95 (1972).

(24) J. P. Birk, *Inorg. Chem.*, **16**, 1381 (1977).

(25) D. R. Rosseinsky and M. J. Nicol, *J. Chem. Soc. A*, 1022 (1968).

(26) F. Freeman et al., *J. Am. Chem. Soc.*, **103**, 1154 (1981).

(27) W. L. Waltz, University of Sasketchewan, unpublished results on the oxidation on a series of cyanometal complexes by the OH radical.

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Molecular Orbital Calculation of Migration Barriers in the LiAlF$_4$ and MgAlF$_5$ Complexes[1]

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Numerous metal halide complexes of the type MAlX$_n$ (M is a mono- or divalent metal; X is a halogen) have recently been studied in the vapor phase by various physicochemical techniques.[2] Experimental evidence has indicated that these complexes exist as edge-bridged structures in which the two metal atoms are bridged by two of the halogen atoms. There has also been some experimental work suggesting that these complexes have face-bridged structures (three halogens in the bridge) or C_s structures (a nonplanar edge-bridged ring). Questions as to the exact structure of these MAlX$_n$ complexes and the mobility of the cation fragment (MX_{n-4}^+) in the complex, which could make structural determination difficult, have not yet been completely resolved.

In previous work we addressed the question of the relative stabilities of corner- (one fluorine in the bridge), edge-, and face-bridged structures of MAlX$_n$-type complexes by carrying out ab initio molecular orbital calculations on LiAlF$_4$,[3] BeAlF$_5$,[4] and MgAlF$_5$.[4] In all three cases the edge-bridged structure was most stable (by 5–25 kcal mol^{-1}) and could be described as an AlF_4^- anion interacting with an MF_{n-4}^+ cation (Li^+, BeF^+, or MgF^+). Others[5] have similarly found the edge-bridged structure for the related LiBeF$_3$ complex to be most stable.

In the work presented here we have calculated energies of points on the pathway for migration of the cation between edge, face, and corner bridges in LiAlF$_4$ and MgAlF$_5$. The motivation for these calculations was to shed light on the following unresolved questions concerning MAlX$_n$ complexes: (1) Are the less stable bridging structures (face and corner bridges) metastable enough to be observed; i.e., what are the barriers for transition from the less stable structures to the equilibrium structure? (2) Does the potential energy of this path allow for easy migration of the cation over the entire anion MX_4^-? (3) Is the potential energy curve in the region of the edge-bridged structure shallow enough to explain the C_s structure observed in electron diffraction studies?

Computational Methods

Calculations were carried out by using standard LCAO-SCF methods[6] with an extended-basis set. The 6-31G basis was used on

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(1) Work was performed under the auspices of the Material Sciences Office of the Division of Basic Energy Science of the Department of Energy.

(2) M. Hargittai and I. Hargittai, "The Molecular Geometries of Coordination Compounds in the Vapour Phase", Elsevier, Amsterdam, 1977.

(3) L. A. Curtiss, *Chem. Phys. Lett.*, **68**, 225 (1979).

(4) L. A. Curtiss and A. Heinricher, *Chem. Phys. Lett.*, **86**, 467 (1982).

(5) (a) V. G. Zakzhevskii, A. I. Boldyrev, and O. P. Charkin, *Chem. Phys. Lett.*, **70**, 147 (1980). (b) E. U. Wurthwein, M. B. Krogh-Jespersen, and P. v. R. Schleyer, *Inorg. Chem.*, **20**, 3663 (1981).

(6) All calculations were performed by using the GAUSSIAN 76 series of programs: J. S. Binkley, R. A. Whiteside, P. C. Hariharan, R. Seeger, J. A. Pople, W. J. Hehre, and M. D. Newton, Program No. 368, Quantum Chemistry Program Exchange, Indiana University.

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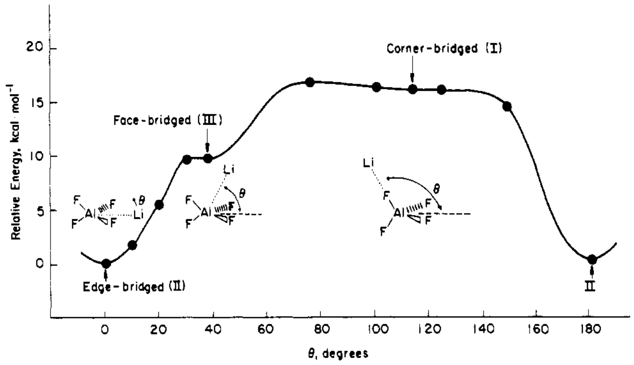

Figure 1. Relative energies for the migration of Li in $LiAlF_4$. Solid circles represent calculated points. Structures I–III were optimized in ref 3. For points between II and III all geometrical parameters were optimized. For points between III and I and between I and II only geometry parameters involving the bridge were optimized. (Energies of other points besides those indicated in the figure were calculated with no geometry optimization to help draw the curve.)

F[7] and Li.[8] Huzinaga's (11s7p) primitive set contracted to (5s4p) according to Dunning and Hay[9] was used on Al, and a (12s10p) primitive set contracted to [4s2p] according to Gole et al.[10] was used on Mg. These basis sets are the same as the ones used in the previous[2,3] geometry optimizations of the corner-, edge-, and face-bridged structures (hereafter referred to as I, II, and III, respectively) of $LiAlF_4$ and $MgAlF_5$.

Results and Discussion

The barriers to lithium migration between the three types of bridges (one, two, and three fluorines) in $LiAlF_4$ were determined by rotating the lithium about aluminum in a plane containing two of the fluorines and bisecting the other two fluorines. As the lithium rotated, the Li–Al distance and the geometry of the AlF_4 fragment were allowed to relax. Rotation of lithium in this manner forms all three structures (I–III) as θ goes from 0 to 180°. This is illustrated in Figure 1. The portion of the potential energy surface investigated here should be representative of the migration path for Li in $LiAlF_4$.

The potential energy curve in Figure 1 shows the relative energies of the calculated $LiAlF_4$ structures for $0° \le \theta \le 180°$. The barrier to migration of lithium for III → II is ca. 0.2 kcal mol^{-1}, the barrier for I → III is ca. 1 kcal mol^{-1}, and there is no barrier for I → II. These barrier values are likely to be upper limits since inclusion of correlation energy tends to decrease barriers.

The small or nonexistent potential wells for the corner- and face-bridged structures in the potential energy surfaces of $LiAlF_4$ means that they are not likely to be metastable enough to be observed. The shallowness of the potential energy curve close to $\theta = 0°$ indicates that the edge-bridged structure may be easily distorted from its C_{2v} structure such that there will be a broad angular distribution of configurations. Consequently, one expects that in measurements such as electron diffraction that average over all configurations the bridge in structure II would be observed as nonplanar. The height of the potential energy curve away from the equilibrium structure (9–16 kcal mol^{-1}) indicates that the cation is not likely to migrate easily very far (e.g., >20°) over the AlF_4^- anion at temperatures up to 2000 K. It should be noted that the height of the potential energy curve could decrease with a more sophisticated calculation (i.e., a bigger basis set or inclusion of correlation energy). Also, in some $MAlX_n$ systems the face- and corner-bridged structures may be closer in energy to the edge-bridged structure (e.g., <5 kcal mol^{-1}). Hence, migration over part or all of the anion would be easier in these cases.

More limited calculations were carried out in the investigation of the $MgAlF_5$ potential energy surface. The MgF fragment was rotated about AlF_4 in the same way as Li was rotated about AlF_4 in $LiAlF_4$. However, the geometries of $MgAlF_5$ for points between structures I, II, and III (relative energies 23.3, 0, and 5.3 kcal mol^{-1}, respectively[4]) were estimated on the basis of the $LiAlF_4$ study and were not optimized. For the transition III → II the barrier was ca. 3 kcal mol^{-1}. This is somewhat higher than the barrier for the same transition in $LiAlF_4$. However, geometry optimization would probably reduce this barrier[11] by 1–2 kcal mol^{-1}. For the transition I → II there is no barrier as in the case of $LiAlF_4$. Hence, by reasoning similar to that used for $LiAlF_4$, we conclude that neither the face- or corner-bridged structure of $MgAlF_5$ is likely to be metastable enough to be observed. However, since the face-bridged structure is only 5 kcal mol^{-1} above the equilibrium structure, it is possible that the cation may be free to migrate over this portion of the potential energy surface.

Conclusions

This study of the energetics for cation migration in $LiAlF_4$ and $MgAlF_5$ indicates that no metastable states for the face- or corner-bridged structures are likely to exist because of the small or nonexistent potential energy wells. The potential energy curve in the region of the equilibrium structure (edge bridged) is shallow, allowing for easy distortion of the planar bridge. Migration of the cation over the entire anion is not likely because of the height of the potential energy curve in regions away from the equilibrium structure.

Registry No. $LiAlF_4$, 15138-76-8; $MgAlF_5$, 23630-60-6; Li^+, 17341-24-1; MgF^+, 21308-25-8.

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(7) W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.*, **56**, 2257 (1972).
(8) J. D. Dill and J. A. Pople, *J. Chem. Phys.*, **62**, 2921 (1975).
(9) T. H. Dunning, Jr., and P. J. Hay, *Mod. Theor. Chem.*, **3**, 1 (1977).
(10) J. L. Gole, A. K. Siu, and E. F. Hayes, *J. Chem. Phys.*, **58**, 857 (1973).
(11) In the case of $LiAlF_4$ optimization of the estimated geometry reduced the energy by up to 2 kcal mol^{-1} for points between II and III.

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The Crown Ether Promoted Base Degradation of *p*-Carborane

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In 1964 Wiesboeck and Hawthorne[1] discovered that degradation of the closo icosahedral carborane 1,2-$C_2B_{10}H_{12}$ by ethanolic KOH produces a novel nido carborane anion, $[7,8\text{-}C_2B_9H_{12}]^-$, whose structure is that of an icosahedron with one vertex removed (Figure 1). Similar treatment of 1,7-$C_2B_{10}H_{12}$ leads more slowly to the isomeric $[7,9\text{-}C_2B_9H_{12}]^-$. In both cases, the boron atom removed is one that is adjacent to both electronegative carbon atoms, which makes the boron more susceptible to nucleophilic attack. Strong base removes the bridging proton from the open face of $[7,8\text{-}C_2B_9H_{12}]^-$ and $[7,9\text{-}C_2B_9H_{12}]^-$ to give nido dianions that can bond to metals in an η^5 fashion.[2] This discovery led to the development of the field of metallacarborane chemistry.

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