trons between the iron ions when one iron is bonded to the oxygen end and one iron is bonded, by means of the lone pair on sulfur, to the sulfur end of the S–O bond. The sulfur atoms, rather than the oxygen, appear to bond DMSO ligands to Pd(II)[8,9] so that transition metal–$SO(CH_3)_2$ bonds are not highly improbable although they are not observed in most of the stable DMSO complexes. The essentially tetrahedral configuration[15] of the oxygen atom, two methyl groups, and the lone pair of electrons around the sulfur atom, would not be expected to permit a sufficient close approach of two S–O bonds, one in each iron complex with the oxygen atoms bonded to the iron ions, so as to make overlap of S═O bonds between metal complexes in an outer-sphere activated complex a ready path for electron conduction.

[15] O. Bastiansen and H. Viervoll, *Acta Chem. Scand.*, **2**, 702 (1948).

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The Thermal Decomposition of Lithium Aluminum Hydride

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The thermal decomposition of lithium aluminum hydride has been investigated utilizing a Perkin-Elmer differential scanning calorimeter. The decomposition was found to occur in three stages; two endothermic and one exothermic change with evolution of hydrogen. A reversible phase change and an exotherm related to sample purity were also noted. The results obtained are at variance in several aspects with studies previously reported.

Introduction

Garner and Haycock[2] investigated the isothermal decomposition of $LiAlH_4$ by measurement of hydrogen evolution and electrical conductivity at several temperatures in the range 100–150°. They found a three-stage reaction, consisting of a rapid initial evolution of gas amounting to less than 1% of the ultimate hydrogen evolved, an accelerating reaction corresponding to the formal equation

$$LiAlH_4 \longrightarrow LiAlH_2 + H_2 \qquad (1)$$

and a slow final step represented formally by

$$LiAlH_2 \longrightarrow LiH + Al + {}^1/_2H_2 \qquad (2)$$

The initial reaction was interpreted as occurring at defects on the surface, which were thought to collapse to a limited number of nuclei from which the decomposition proceeds by a specific interface reaction, yielding the observed cubic time dependence of the second stage. The behavior of the last stage was found to be erratic and was not investigated in detail.

Mikherva, Selivokhina, and Kryukova[3] investigated $LiAlH_4$ utilizing differential thermal analysis with simultaneous collection and measurement of evolved hydrogen. In any such temperature-scanning technique, the influence of steadily increasing temperature is superimposed on the effect of increasing reaction time, so that reactions which are essentially consecutive under isothermal conditions occur at successively higher temperatures in the program. The apparent reaction temperatures for the individual steps will depend upon their reaction rates, their activation energies, and the instrumental temperature-scanning rate. At sufficiently fast scanning rates, consecutive reactions are often "resolved" on the temperature axis, and the general character of the reaction sequence is thereby obtained in an experiment of short duration which is comparatively easy to interpret. Mikherva, *et al.*, report three endothermic maxima in their thermograms, corresponding to evolution of one-half the theoretical hydrogen at 154–161°, one-quarter at 197–227°, and the remaining one-quarter at 580–586°.

We have re-examined the thermal decomposition of $LiAlH_4$, utilizing a Perkin-Elmer differential scanning calorimeter (DSC-1).[4] This instrument provides direct differential power read-out as opposed to differential temperature, and areas consequently are directly related to transition energies. This facility, coupled with the integral thermal conductivity effluent analyzer, allows an unambiguous interpretation of the thermal events accompanying the decomposition of $LiAlH_4$.

Experimental

Lithium aluminum hydride, obtained from Metal Hydrides, Inc., Beverly, Mass., was recrystallized from ethyl ether and dried under vacuum at 60–70°. Elemental analyses of the recrystallized product indicated a minimum purity of 98% $LiAlH_4$, with less than 0.5% residual ether. Samples of 1–4 mg. were accurately weighed with a Cahn Model G electrobalance in aluminum dishes, which were standard sample containers supplied with the Perkin-Elmer differential scanning calorimeter. With an empty pan in the reference holder, the sample was placed in the instrument, both holders covered with loosely fitting gold caps, and the entire assembly enclosed with the O-ring-sealed cover provided with the instrument. The enclosed holder space was flushed continuously with an inert gas (usually argon) prior to and during the scan. The effluent gas was monitored with the thermistor thermal conductivity detector provided with the instrument. The thermal read-out was recorded with a Texas In-

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[1] W. R. Grace and Co., Washington Research Center, Clarksville, Md.

[2] W. E. Garner and E. W. Haycock, *Proc. Roy. Soc.* (London), **A211**, 335 (1952).

[3] V. I. Mikherva, M. L. Selivokhina, and O. N. Kryukova, *Proc. Acad. Sci. USSR, Chem. Sect.*, **109**, 439 (1956).

[4] E. S. Watson, M. J. O'Neill, J. Justin, and N. Brenner, *Anal. Chem.*, **36**, 1233 (1964).

struments Recti/Riter recorder and the thermal conductivity response with a Leeds and Northrup Speedomax Type G recorder. Areas were subsequently measured with a planimeter.

Temperature and area calibration were checked with high-purity indium taken to have a melting point of 156° and a heat of fusion of 6.8 cal./g. The "no sample" base line was determined prior to each run with empty pans in both sample and reference holders, but with conditions otherwise identical.

Results and Discussion

A typical thermogram and the simultaneous effluent gas trace obtained on a 2.34-mg. sample scanned at 10°/min. to 220° and then at 20°/min. (for better resolution) is shown in Figure 1. The averages of the data from several scans and interpretations are summarized in Table I. In agreement with Mikherva, *et al.*, three endotherms are observed, but two distinct and well-resolved exotherms are also noted. In addition, the first endotherm, peaking at 170°, is not associated with the evolution of hydrogen, as stated by these authors, but is in fact a reversible phase change. This was demonstrated in this work by reversing the scan to the cooling mode after passing through the transition. This is shown in Figure 2, where the scan was reversed at 176° to produce an exotherm of identical magnitude occurring at the lower temperature of 154° due to supercooling. Reheating the sample reproduces the original endotherm.

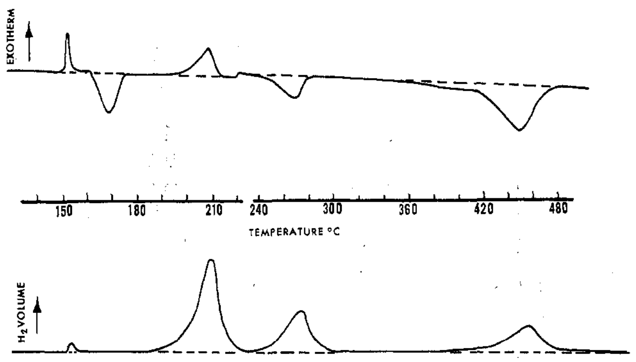

Figure 1.—Differential scanning calorimetric and effluent analysis of $LiAlH_4$. Sample weight 2.34 mg.; heating rate 100–220° at 10°/min., 220–500° at 20°/min.

TABLE I

OBSERVED THERMAL EVENTS IN THE DIFFERENTIAL SCANNING CALORIMETRY OF $LiAlH_4$

Range, °C.	ΔH, cal./g.	% H_2 evolved	Interpretation[a]
148–158	−14	1.1	$>AlOH + >AlH \longrightarrow >Al—O—Al< + H_2$
160–177	76	. . .	Phase transition
187–218	−64	51.2	$LiAlH_4 \longrightarrow LiAlH_2 + H_2$
228–282	56	25.6	$LiAlH_2 \longrightarrow LiH + Al + {}^1/_2H_2$
370–483	176	22.0	$LiH \longrightarrow Li + {}^1/_2H_2$

[a] The molecular formulas shown indicate only the over-all stoichiometry of the reactions and are not meant to imply the existence of specific molecular entities in the reaction products.

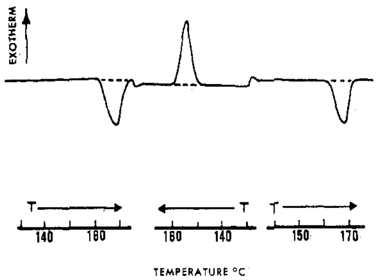

Figure 2.—Differential scanning calorimetric analysis of $LiAlH_4$, heating and cooling. Sample weight 2.28 mg.; heating rate 10°/min.; cooling rate 10°/min.

A particularly interesting observation is the existence of the first exotherm peaking at 153°. It seems probable that this is to be associated with the initial decomposition found by Garner and Haycock and considered by them to be a surface reaction, initiating the subsequent primary decomposition. The H_2 evolution associated with this reaction is small, approximately 1% of the theoretical total, as found by Garner and Haycock. However, the reaction clearly cannot be ascribed to surface decomposition of the type represented by eq. 1, since the first exothermic thermal effect per mole is an order of magnitude greater than the second, which represents the bulk of the decomposition by this route. To check the possibility that the gas evolved during the 153° exotherm was not hydrogen, but possibly associated with etherate decomposition products, the decomposition was run with helium as flushing and carrier gas. The relative areas of the effluent peaks remained unchanged, indicating that the evolved gas at 153° was, in fact, H_2. Considering the difficulty of obtaining and maintaining absolute purity of a preparation of $LiAlH_4$ and also the magnitude of the heat effect, an impurity reaction of the type

$$>Al\text{-}OH + H\text{-}Al< \longrightarrow >Al\text{-}O\text{-}Al< + H_2 \qquad (3)$$

was considered likely to account for the existence of the first exotherm. This was confirmed by examination of samples deliberately exposed to the atmosphere where the first exotherm increased in magnitude with the exposure. At high levels of contamination, the relationship between evolved hydrogen and observed heat deviated from that found for low levels, no doubt because of increasing complexity and/or incompleteness of the reaction. In any event, the initial exotherm clearly appears to be associated with sample impurity, and the kinetic conclusions drawn by Garner and Haycock with respect to the initial decomposition are therefore in question.

While the reaction heats given in Table I are experimentally reproducible to within a few per cent, it is doubtful if they are of much thermodynamic usefulness, since the physical states of the reaction products are not known. It should be pointed out, however, that the determination of the reaction heat associated with the initial reaction should prove to be an analytically useful means of assessing the purity of $LiAlH_4$ preparations.

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