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GAS EVOLUTION PROFILES AND DIFFERENTIAL THERMAL ANALYSIS*

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ABSTRACT

The isothermal decomposition curves of solids which decompose to yield a new solid plus a gas have shapes which are dependent on the mechanism of nucleation, the shape of the nuclei, and the nature of the growth of the nuclei. The decomposition-time curves of these types of decomposition reactions have been classified into three types[1] corresponding to rapid initial decomposition, an induction period before decomposition and a small initial decomposition followed by an induction period then a sigmoid shaped curve. In practice the sigmoid shape curves may be modified by self-heating, self-cooling, and catalytic effects which may change the nature of the decomposition curves. In addition the possibility of consecutive decomposition reaction causing departure from the sigmoidal nature may be encountered if the decomposition temperature is sufficiently high to provide an appreciable rate for a consecutive reaction.

INTRODUCTION

The importance of gas evolution analysis has been noted in the past and the detection of evolved gases by thermal conductivity cells[2], mass spectrometers[3], and gas chromatographs[4] has revealed an unexpected complexity even in apparently simple chemical systems. In this work we report several results of the simultaneous measurement of differential thermal analysis curves and the integral gas evolution profiles.

Information from gas evolution profiles provides information which is not readily apparent from the corresponding differential thermal analysis curves since the inherent response time constants of thermal instrumentation inhibit the observation of very fast reactions.

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EXPERIMENTAL

Experimental measurements with a differential thermal analysis apparatus which was assembled in the laboratory. An F & M Model 240 M temperature programmer was used in this study. The oven was constructed from hemicylindrical heating elements obtained from the Hevi-Duty Electric Company. Asbestos fiber was used for insulation. Sample holders were machined from stock aluminum to provide a cylinder 2.625" diameter, 3.5" length. Two holes were drilled one-half inch from the center of the block to hold Kimax culture tubes (6 × 50 mm) for the sample and reference. Additional holes were for the programmer thermocouple and auxiliary temperature sensors as required. Thirty gauge chromel–alumel thermocouples were used for the differential thermocouple assembly. A Leeds and Northrup DC microvolt amplifier Model No. 9835B was used to amplify the signal from the differential thermocouple. The amplified signal was recorded with a Moseley Model 2 S x–y recorder. The sample culture tube was sealed to a long piece of 8-mm Pyrex tubing containing a capillary side arm through which one arm of the differential thermocouple was inserted. The sample was placed in the bottom of the culture tube through the top of the tube which was attached to the vacuum line with an 18/7 ball joint. The thermocouple was sealed into the apparatus with Apiezon W hard black wax. A similar dummy reference tube was placed in the heating block although it was not connected to the vacuum line and was used to balance the heat capacity of the sample and reference. The change in pressure with time (temperature) was measured with a Statham Model TA-203-TC-10-35V pressure transducer. The signal from the transducer was recorded with a Sargent Model SR recorder.

Materials and supplies

The sample and reference tubes contained about 0.1 g of material when loaded. Inert fused alumina from Norton Company (90 mesh) was used as reference material. Lithium aluminum hydride (95% + purity) and lithium aluminum deuteride were obtained from Metal Hydrides, Inc. They were crushed in a mortar before use. Sodium aluminum hydride was obtained from the Ethyl Corporation. Cab-o-sil (thixotropic gel powder) was obtained from Packard Instrument Company, Inc. Aluminum oxide was obtained from Fisher Scientific Company.

Procedure

Samples were placed in the tube attached to the vacuum line and evacuated to several mm pressure. The vacuum line was alternately filled with helium and evacuated so that the atmosphere above the sample was ultimately helium at a pressure of approximately 3–5 mm of Hg.

DISCUSSION

Simple sigmoid shaped curves for decomposition reactions conducted under isothermal conditions should in principle have the same appearance as those obtained from differential thermal analysis thermogram upon integration of the area under the curve. The prime difference when such measurements are made in a programmed temperature experiment is that the sigmoidal shaped curve has a larger slope at its midpoint.

With the experimental apparatus described in this paper the same shaped curve is indeed obtained from gas evolution or from integrated differential thermograms in most cases. Since the decomposition proceeds at an interface from the edges of the cylindrical sample tubes into the container the gas evolution curves usually appear at an apparent lower temperature which is dependent on the heating rate. The faster the heating rate the greater the separation between the two sigmoidal shaped curves. Such is the case for the thermal decomposition of $KMnO_4$.

When fast decomposition reactions occur that are not easily followed by thermal methods a distinct advantage is obtained in following the reaction path by the recording manometer approach since abrupt changes in rates of decomposition rate are readily observed. Block and Gray[5] reported thermograms for lithium aluminum hydride in which simultaneous differential scanning calorimetry scans and gas evolution profiles were reported. They noted two exothermic and three endothermic events in their thermograms. Associated with four of the thermal events were gas evolution. This was measured with a thermal conductivity effluent analyzer which by its very nature would not exactly follow the thermal decomposition profiles. Considerable effort was expended by the above workers in obtaining a very pure sample of lithium aluminum hydride. An endothermic observation at 160–177 °C was attributed to a phase transition. They identified the first endotherm to a reaction involving AlOH bonds with Al–H bonds in a hydrogen liberation reaction. In a subsequent paper, McCarty, Maycock, and Verneker[6] verified prior observations yet noted some dissimilarities of importance. Their work was conducted with 5-mg samples on the Mettler vacuum recording thermoanalyzer. In a recent publication the solid state reaction of lithium hydride and aluminum has been studied clarifying the details of the final endotherm in the thermogram of lithium aluminum hydride[7].

In this investigation a purposeful study was made of lithium aluminum hydride as received from the supplier. This was nominally 95% pure. This was studied directly or mixed with aluminum oxide or cab-o-sil in order to evaluate its effect as a diluent on the decomposition. Similarly a sample of aged lithium aluminum deuteride was studied. Isothermal decomposition reactions were followed and the usual sigmoidal shaped decomposition curves were obtained on the hydride and the deuteride. The programmed temperature gas evolution profile recordings reveal several unique differences from those measured under isothermal conditions. The usual sigmoid shaped curve is not obtained but a generalized type of curve as shown in Fig. 1 was always observed. Upon heating samples from room temperature a gradual pressure increase was noted which gradually accelerated until there was an instantaneous evolution of hydrogen. This was followed by a slower decomposition until the pressure increase corresponded to the loss of two hydrogen atoms to a level of decomposition corresponding to $LiAlH_2$. The decomposition curve then progressed into the usual sigmoid shaped curve corresponding to the further decomposition reaction $LiAlH_2 \rightarrow LiH + \frac{1}{2}H_2$. It is known that this equation does not represent a chemical reality. It is more realistic to identify this reaction according to the equation[8,9] $3\ LiAlH_4 \rightarrow Li_3AlH_6 + 2Al + 3H_2$ which would also correspond to the amount of hydrogen liberated. These pressure profiles differ from those reported by Mikheeva and Arkhipov for a very pure $LiAlH_4$. Lithium hexahydridoaluminate decomposes without melting above 210°C and no solvent has been reported for it[10]. It decomposes in air without ignition and is hydrolyzed with water with ease. The range of temperatures investigated in this work did not include the region corresponding to the solid state decomposition reaction of lithium hydride with aluminum.

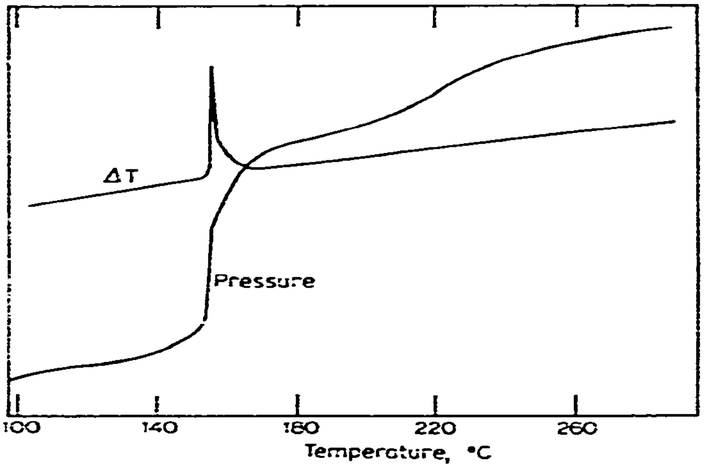

Fig. 1. Manometric-differential thermal analysis evaluation of lithium aluminum hydride.

The decomposition of lithium aluminum hydride is best represented by the following equations:

(1) $LiAlH_4 \xrightarrow{\text{surface}} H_2$

(2) $3LiAlH_4 \xrightarrow{\Delta} Li_3AlH_6 + 2Al + 3H_2$

(3) $Li_3AlH_6 \xrightarrow{\Delta} 3LiH + Al + 3/2\ H_2$

(4) $LiH + (Al)_x \xrightarrow{\Delta} [Li(Al)_x] + H_2$

Ashby has reported that Li_3AlH_6 and Na_3AlH_6 are produced by the thermal decomposition of the respectus tetrahydridoaluminates[11] but that a direct synthesis was not successful from a Li–Al mixture. Similarly Mikheeva and Arkhipov have noted that Li_3AlH_6 is a product in the sequence of decomposition reactions in the total decomposition of $LiAlH_4$[9].

It is clear that very reactive substances such as $LiAlH_4$ rapidly change in their thermal characteristics as they age. The differential thermal analysis curves for aged $LiAlH_4$ samples are substantially different from purified preparations such as were investigated in prior reports[5,6,9]. Simultaneous thermogram and gas evolution profile measurements on aged samples reveal that the endotherms previously noted do not appear and that the programmed temperature gas evolution profiles contain an abrupt gas evolution step not observed with purified samples. This is apparent with both $LiAlH_4$ and $LiAlD_4$ samples. This behavior suggests that a surface catalyst is created in the aging process for the hydride. Mikheeva and Arkipov[9] suggest that the initial decomposition results from adsorbed oxygen or water in contradiction with prior work[5]. With cab-o-sil a silica gel, mixed with lithium aluminum hydride or deuteride, violent reactions with ignition resulted at this initial decomposition temperature. The same result was observed when thermograms of the mixture were obtained in an inert helium atmosphere. This is consistent with the postulate that adsorbed water would cause the initial decomposition. A less violent effect was observed when ordinary aluminum oxide was used as a diluent. It is attractive to hope that a simple method could assay for purity of $LiAlH_4$ preparations as suggested previously but the complications of changing characteristics of both thermograms and gas evolution profiles must be carefully evaluated. It should be noted that $NaAlH_4$, a melting complex hydride shows a similar abrupt gas evolution as an onset to melting and the gas evolution profile is even more complicated because of the increase in vapor pressure of the melt.

A logical inference of these observations is that the phase transition identified by Block and Gray[5] results in the exposure of a fresh $LiAlH_4$ surface to a surface "catalyst" in aged samples with a resultant abrupt evolution of hydrogen. This reaction involves appreciable self heating of the sample which further aids in the decomposition and obscures the endotherm previously identified. The decomposition can in fact proceed beyond the Li_3AlH_6 stage to total decomposition on heating if the "catalyst" is in sufficient abundance.

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