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THE REACTION OF LITHIUM ALUMINIUM HYDRIDE WITH CARBON DIOXIDE OR SODIUM BICARBONATE

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Abstract—The reaction of $LiAlH_4$ with CO_2 or $NaHCO_3$ at elevated temperatures has been investigated. Methane and ethylene are the primary products of each reaction. These molecules are probably the "explosive" reaction products formed when CO_2 fire extinguishers are used on $LiAlH_4$ fires.

Recently several letters have appeared in the literature discussing the hazards of lithium aluminium hydride ($LiAlH_4$ or LAH) fires.[1-3] It was reported that burning LAH pellets could not be quenched in a nitrogen atmosphere and an intert gas such as argon was required to extinguish the fire safely. It was also noted that the use of a sodium bicarbonate or carbon dioxide (CO_2) fire extinguisher to extinguish a LAH fire formed "explosive" reaction products.[2-4] LAH is a common reducing reagent for both organic and inorganic reactions.[5,6] In addition, there has been a considerable amount of interest generated in C_1 chemistry.[7-10] The reaction of CO and CO_2 with H_2 in the presence of metal reducing catalysts can produce a variety of organic molecules ranging from methane to gasoline hydrocarbons.[7] Since LAH is such a good reducing agent and there are hazards in trying to extinguish a LAH fire, an investigation of the reaction of LAH with CO_2 and with $NaHCO_3$ was undertaken. This paper presents the results of this investigation.

EXPERIMENTAL

The apparatus used to investigate the LAH reactions has been described in detail previously.[11,12] Briefly, the reactions were carried out in a quartz tube attached to an MDC Manufacturing Company stainless steel 4-way cross vacuum flange. Two opposing sides of the flange were equipped with KBr windows to make an infrared gas cell. The entire system was maintained under vacuum by a liquid nitrogen trap, 2 in. oil diffusion pump and a rotary vacuum pump. An uncalibrated thermocouple gauge was used to monitor the pressure in the system. This cell was placed in the sample compartment of a Nicolet MX-1 Fourier Transform IR Spectrometer (FTIR). The spectra were taken using 1 min scans at 1 cm^{-1} resolution as the reaction progressed. After completion of the reactions, the trapped gases were either allowed to flow back into the cell so spectra could be retaken or they were collected in a mass spectrometer sampling bulb. In most cases the IR spectrum was sufficient to identify the reaction products, however, mass spectra, taken on a Varian EM-600, were occasionally used to confirm the product assignments.

All of the experiments were performed in essentially the same way. LAH or mixtures of LAH and various reactants were placed in the quartz tube and the system was evacuated to 0.1 Pa pressure. The tube was resistively heated with a nichrome wire. Sufficient CO_2 was added to the reaction mixture to produce a combined total pressure of 10^2 Pa and the spectrum was taken as the reaction proceeded.

RESULTS AND DISCUSSION

From the reaction of $LiAlH_4$ with CO_2, the following products were identified from the IR absorption bands (cm^{-1}) cited: CH_4 (3016, 1305); C_2H_4 (3100, 949); CO (2144). At approximately 400 K, small amounts of methane (CH_4) were formed. When the quartz tube was heated to 600 K, CH_4 and ethylene (C_2H_4) were rapidly formed. After prolonged heating which partially depleted the LAH, carbon monoxide bands also appeared in the spectrum. Reactions involving CO_2 and CO in solution with LAH have been investigated previously.[13-16] Apparently, the reaction products from solution are very different from the gas/solid reaction products found here. Cox *et al.*[16] reported that methane and carbon monoxide were not present as reduction products of the solution reaction. However, while carrying out methanolysis reactions using CO and LAH in solution, Martin *et al.* determined that methane was one of the reaction products.[14] The lower reaction temperatures (~ 373 K) of these solution reactions, solvent effects, stirring, etc. apparently can combine to yield a variety of different products. In the gas/solid reactions performed here, only CO, CH_4 and C_2H_2 have been observed as the reaction products.

The second experiment performed was the reaction between sodium bicarbonate and LAH. In this experiment the LAH and $NaHCO_3$ were mxied ($\sim 50/50$, v/v) and placed in the quartz tube. This mixture was heated and the spectra were taken. As the mixture was warmed to 325 K, bands for H_2O (1600 cm^{-1}) and CO_2 (2350, 667 cm^{-1}) could be observed. As the temperature was increased, the bands

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for water decreased and bands for methane (3016, 1305 cm^{-1}) and ethylene (3100, 949 cm^{-1}) appeared in a manner similar to the CO_2/LAH experiments. $NaHCO_3$ is known to decompose at ~ 325 K to form H_2O and CO_2[17] which readily explains the observation of these bands in the spectra at these temperatures. The other products resulted from the reaction of CO_2 and LAH.

Differential Thermal Analysis (DTA) indicates that LAH decomposes through several steps.[18] The first of these occurs at 421–431 K where part of the hydrogen is evolved. As the LAH is heated to higher temperatures (~ 500–555 K) significant amounts of H_2 are evolved as the compound decomposes. Since no CH_4 was observed at temperatures lower than ~ 400 K, it was assumed that the reactions of LAH with CO_2 and $NaHCO_3$ must first proceed with the partial decomposition of the LAH to form finely divided Al metal. This Al would then react with CO_2 to form CO and aluminium oxide. The CO must then further react to form a CH_2 radical. This radical could either react with H_2 to form CH_4 or with additional CH_2 to form C_2H_4. To test this hypothesis another experiment was performed. In this experiment CO_2 and H_2 were passed over finely divided aluminium powder placed in the quartz tube. The tube was heated and the spectrum taken. No reaction was observed until the tube was heated to 650–800 K. At these temperatures the bands for CO_2 slowly disappeared and bands for CH_4, C_2H_4, CO and H_2O grew into the spectrum. It is interesting that H_2O was produced in this experiment since it was not observed in the LAH reactions with CO_2. One possible explanation of this observation is that any H_2O produced in the previous experiments rapidly reacted with LAH and thus was not observed. The Al formed from the thermal decomposition of LAH is expected to be more finely divided and hence more reactive than the Al powder used in these experiments. These results suggest that Al metal takes part in the reaction mechanism. Since H_2O was observed in this set of reactions, it is not certain if Al functions as a reactant or a catalyst. In either case, the first step of the reaction probably is

$$Al + CO_2 \rightarrow \text{"AlO"} + CO.$$

This is not unlike the mechanism proposed by Fontijn *et al.* for the reaction of Al atoms and CO_2.[19] This "AlO" may then react with hydrogen to reform the Al and H_2O or it may further react with CO_2 to form Al_2O_3. The failure to observe clearly Al_2O_3 suggests that the former may have occurred. However, since the total amount of Al_2O_3 formed is expected to be small, this cannot be taken as definite proof that Al is acting as a catalyst. The role of H_2 gas in the mechanism is also not known with certainty. It is likely that some of the hydrogenations occur on the Al surface. The reaction of hydrogen in the gas phase may also occur for some steps in the mechanism. The steps where each is the case could not be clearly established.

Bellama and MacDiarmid investigated the solid phase reactions of SiO_2, GeO_2, P_2O_5, As_2O_3 and Sb_2O_3, with LAH.[20] They found that these reactions produced the various hydrides of these elements. In addition, they reported that some of their samples of LAH were contaminated with small quantities of diethylether and ethylene since they also observed these molecules in their system. Based on the results of the experiments performed here, it appears reasonable to suggest that they may have actually observed products from the reaction of the LAH with residual CO_2 in the reaction vessel. To test this hypothesis, one of their experiments was repeated using this apparatus. In this experiment SiO_2 and LAH were mixed (~ 50/50, v/v), placed in the quartz tube, and heated. In addition to the expected silane (SiH_4) bands at 2188 and 909 cm^{-1}, bands for methane and ethylene were clearly visible in the spectrum even though no CO_2 was passed over this reaction mixture. No bands were observed which could be assigned to diethyl ether. It does, however, appear that Bellama and MacDiarmid may also have observed the reaction of LAH with residual CO_2 in their reaction vessel. Methane probably was not observed in their experiments because of a failure to trap it. Any methane produced may have been pumped out of their system with the evolved hydrogen.

CONCLUSION

Based on the results of these experiments, a reaction scheme may be written for the gas/solid reaction of CO_2 and LAH.

(1) $LiAlH_4 \xrightarrow{\sim 500\,K} Al + LiH + 3H_2$.

(2) $2Al + 3CO_2 \xrightarrow{\sim 500\,K} Al_2O_3 + 3CO$.

(3) $2Al + 3H_2 + 3CO \rightarrow Al_2O_3 + 3CH_2$.

(4) $CH_2 + H_2 \rightarrow CH_4$.

(5) $CH_2 + CH_2 \rightarrow C_2H_4$.

The formulas shown are meant to indicate only the overall stoichiometry of the reaction. As stated previously, it is not certain that Al_2O_3 forms directly from the reaction of Al and CO_2. It is possible that it could be produced by the sequence

(a) $Al + CO_2 \rightarrow \text{"AlO"} + CO$.

(b) $\text{"AlO"} + H_2 \rightarrow H_2O + Al$.

(c) $4H_2O + LiAlH_4 \rightarrow LiOH + Al(OH)_3 + 4H_2$.

(d) $2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$.

Since no H_2O was observed in the LAH reaction and the final products are largely the same, the simpler overall scheme (not involving H_2O) is proposed as the actual reaction sequence. Sapienza *et al.* have proposed a mechanism for the formation of methanol from the reaction of CO_2 and H_2 on metal oxide surfaces.[21] They propose that CO_2 is dissociated to CO and O which are chemisorbed on to the surface of the metal oxide. In the presence of H_2 the CO is reduced to methanol. No bands for methanol were observed in the spectra from these epxeriments. Whether the absence of methanol bands indicates that no Al_2O_3 is formed or that the H_2 is largely depleted by the time it forms cannot be determined from these experiments. CH_2 radical also was not observed. Its presence is inferred from the observation of only ethylene and methane as the reaction products. Additionally, the decomposition products of LAH have not been well characterized. Thus, while the proposed reaction scheme accounts for all of the products, many details of the mechanism still have not been established.

Based on these experiments, it appears that the "explosive" reaction products reported for the burning LAH/CO_2 reaction are methane and ethylene. Both molecules would react explosively with oxygen in the air if ignited. A CH_4/C_2H_4/Air mixture could easily be ignited by the heat from the burning LAH. Additionally, when $NaHCO_3$ is used to put out a LAH fire, H_2O is formed. Normally this would be desirable for a fire extinguisher. In this case, however, it would only serve to aggravate the situation since LAH and H_2O react violently.

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