$LiAlH_4$ and $LiBH_4$ as Reagents for the Formation of Lithium Intercalation Compounds of the Metal Oxides, V_2O_5, WO_3, U_3O_8, and MoO_3

Simon J. Hibble, Peter G. Dickens, and Jonathan C. Evison
Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, U.K.

$LiAlH_4$ and $LiBH_4$, in solution in ethoxyethane, are shown to act as lithiating agents for the production of lithium intercalation compounds, Li_xMO_n, from polycrystalline samples of the oxides V_2O_5, WO_3, MoO_3, and U_3O_8.

This communication supplements an earlier very brief report by Glemser, Hauschild, and Bimmerman[1] that the action of $LiAlH_4$ on the metal oxides MO_n (M = Mo, W, V) followed by hydrolysis leads to the formation of hydrogen intercalation compounds H_xMO_n (though no analytical data were given). We believe this novel reaction of $LiAlH_4$ and $LiBH_4$, under anhydrous conditions, could be of broad application. We have found that $LiAlH_4$ and $LiBH_4$ in ethoxyethane react with V_2O_5, WO_3, MoO_3, and U_3O_8, under these conditions to give the non-stoicheiometric lithium intercalation compounds, $Li_xV_2O_5$ $(0.1<x<1.0)$,[2,3] Li_xWO_3 $(0<x<0.7)$,[4] Li_xMoO_3 $(0<x<1.6)$,[5] and $Li_xU_3O_8$ $(0<x<2.1)$.[6]

Table 1. *X*-Ray powder data for $Li_{0.45}V_2O_5$ 0.06Al.[a]

I	$d_{obs.}$/Å	$d_{ref.}$/Å $Li_{0.45}V_2O_5$	*h*	*k*	*l*
m	5.725	5.662	2	0	0
s	4.502	4.512	0	0	1
w	4.175	4.192	1	0	1
s	3.404	3.406	1	1	0
m	2.895	2.909	3	0	1
m	2.858	2.855	4	0	0
m	2.603	2.602	3	1	0
w	2.340	(aluminium	1	1	1)
w	2.037	(aluminium	2	0	0)
w	1.781	1.782	0	2	0
w	1.431	(aluminium	2	2	0)

[a] Refined lattice parameters: $a = 11.42(1)$, $b = 3.562(2)$, $c = 4.48(1)$ Å; *cf.* $Li_{0.45}V_2O_5$ (ref. 3): $a = 11.413(5)$, $b = 3.565(2)$, $c = 4.52(1)$ Å.

Table 2.

Reaction	Product composition	Phases present[a]
WO_3 + xs $LiAlH_4$	$Li_{0.27}WO_3$ 0.06Al	Li_xWO_3 tetragonal $x = {\sim}0.1$ + cubic $x = {\sim}0.4$ + Al
V_2O_5 + 0.45 $LiAlH_4$	$Li_{0.44}V_2O_5$ 0.11Al	$Li_{0.44}V_2O_5$ + Al
V_2O_5 + 0.88 $LiAlH_4$	$Li_{0.92}V_2O_5$ 0.11Al	$Li_{1.01}V_2O_5$ + Al
U_3O_8 + 0.88 $LiAlH_4$	$Li_{0.90}U_3O_8$ 0.24Al	$Li_{0.90}U_3O_8$ + Al
MoO_3 + 0.5 $LiAlH_4$	$Li_{0.52}MoO_3$ 0.52Al	$Li_{0.40}MoO_3$ + Al
MoO_3 + 1.8 $LiAlH_4$	$Li_{1.41}MoO_3$ 1.46Al	weak lines + Al
V_2O_5 + 0.69 $LiBH_4$	$Li_{0.69}V_2O_5$	$Li_{0.45}V_2O_5$ + $Li_{1.01}V_2O_5$
MoO_3 + 0.75 $LiBH_4$	$Li_{0.77}MoO_3$	
WO_3 + 0.46 $LiBH_4$	$Li_{0.33}WO_3$	$Li_{0.33}WO_3$ cubic
MoO_3 + 1.15 $LiAlH_4$	$Li_{1.13}MoO_3$ 0.15Al	(short reaction time 4 hours)

[a] Identified from powder *X*-ray data (refs. 3—6).

Ethoxyethane solutions of $LiAlH_4$ and $LiBH_4$, approximately 0.2 M, were added to powdered samples of the metal oxides under dry nitrogen. The reactions with $LiAlH_4$ solutions were rapid, an immediate colour change occurring along with an evolution of gas. For V_2O_5, WO_3, and U_3O_8, gas evolution appeared to have ceased after 2 hours but for MoO_3 bubbles of gas were still being formed for up to 96 hours. After 6—96 hours the supernatant was removed and the samples washed with dry diethyl ether. The final solid products contained no unreacted oxides and were uniformly coloured. No metal from the starting oxides was found in the supernatant or washings. For V_2O_5, WO_3, and U_3O_8, the products were identified conclusively as known lithium intercalation compounds by means of powder *X*-ray diffraction. Table 1 shows sample *X*-ray data for the reaction of $LiAlH_4$ with V_2O_5. In addition to the lithium intercalation compound, powder *X*-ray diffraction showed that aluminium metal was present in the products. The solid products were analysed for Li, Al, heavy metal, C, and H and the mean oxidation states of the heavy metals determined by titration.[7] Only traces of C and H were found. Reactions with MoO_3 produced solid products which were poorly-crystalline, although their powder *X*-ray patterns had some lines in common with the known Li_xMoO_3[5] phases. Chemical analysis showed that these products too were the lithium intercalation compounds although larger quantities of aluminium metal contaminated the product. The aluminium present in the products appeared always as aluminium metal and not chemically combined within the oxide matrix. The amount of aluminium in all the products increased with the reaction time. Table 2 gives some examples of the composition of the products.

The initial reactions with $LiBH_4$ were less rapid than for $LiAlH_4$ although the reaction with MoO_3 was complete after 2 hours. Powder *X*-ray diffraction for these products showed only the lithium intercalation compounds and analysis figures gave excellent agreement between the lithium content from atomic absorption and the overall state of reduction of the product. $LiBH_4$ appears to be a potentially more useful reagent for the preparation of pure lithium intercalation compounds than $LiAlH_4$. Some examples of the reactions and products are given in Table 2.

Reaction (1) summarises our observations with $LiAlH_4$. This is followed by a decomposition of the aluminium hydride to give aluminium metal and hydrogen, equation (2). Some aluminium metal was always found in the products but the second reaction appeared to be very slow for all but MoO_3. Even for MoO_3 the second reaction was slower than the first (note the composition of the product for the short reaction time in Table 2) but long reaction times deposited an amount of aluminium metal equivalent to the lithium inserted into the oxide.

For $LiBH_4$, analysis of the products (Table 2) shows that only the single reaction (3) occurs.

$$x\mathrm{LiAlH_4(sol)} + \mathrm{MO}_n\mathrm{(s)} \rightarrow \mathrm{Li}_x\mathrm{MO}_n\mathrm{(s)} + \mathrm{AlH_3(sol)} + x/2\ \mathrm{H_2(g)} \quad (1)$$

$$\mathrm{MO}_n = \mathrm{V_2O_5},\ \mathrm{WO_3},\ \mathrm{U_3O_8},\ \text{and}\ \mathrm{MoO_3}$$

$$2\mathrm{AlH_3(sol)} \rightarrow 2\mathrm{Al(s)} + 3\mathrm{H_2(g)} \quad (2)$$

$$x\mathrm{LiBH_4(sol)} + \mathrm{MO}_n\mathrm{(s)} = \mathrm{Li}_x\mathrm{MO}_n\mathrm{(s)} + \mathrm{BH_3(sol)} + x/2\ \mathrm{H_2(g)} \quad (3)$$

$$\mathrm{MO}_n = \mathrm{V_2O_5},\ \mathrm{WO_3},\ \text{and}\ \mathrm{MoO_3}$$

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