Vanadium Nitrides: Reactions of Vanadium Oxides with Lithium in the Presence of Nitrogen

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The reaction of vanadium oxides with liquid lithium containing dissolved nitrogen provides a method for the preparation of nitrides of vanadium. The oxides V_2O_5, VO_2, V_2O_3, and VO are reduced by liquid lithium to the metal. Depending on the quantity of nitrogen available, further reaction then occurs to give the α phase solid solution of nitrogen in vanadium, the nitrides V_3N and VN, or the ternary nitride Li_7VN_4.

TERNARY oxides have been observed as products in reactions between liquid sodium [1] or potassium,[2] and transition-metal oxides. Such compounds are usually formed when there is a small difference in free energy of formation between the alkali-metal oxide and the transition-metal oxide. The behaviour of transition-metal oxides in liquid lithium differs from that in the other alkali metals in that lithium oxide has a free energy of formation much larger than many transition-metal oxides. Direct reduction of the transition-metal oxide to the metal and lithium oxide therefore takes place. In other alkali-metal reactions, the alkali-metal oxide is capable of further interaction with the transition metal to form ternary oxides, but the increased stability of lithium monoxide precludes such interactions taking place in liquid lithium with the majority of transition elements.

Lithium is unique amongst the alkali metals in that the solubility of nitrogen [3] is such that considerable quantities of the non-metal may be dissolved in liquid lithium. Carbon [4] and hydrogen [5] also possess appreciable solubilities in lithium. Reactions may also be carried out between these non-metals and transition elements, in liquid lithium, since the enthalpies of formation of lithium nitride ($-\Delta H_{298} = 197{\cdot}5$ kJ/g. atom N), lithium carbide ($-\Delta H_{298} = 58{\cdot}2$ kJ/g. atom C), and lithium hydride ($-\Delta H_{298} = 90{\cdot}4$ kJ/g. atom H) are much lower than that of lithium oxide ($-\Delta H_{298} = 595{\cdot}8$ kJ/g. atom O).

Here the reactions of the vanadium oxides with liquid lithium containing a very small quantity of nitrogen are first described. Direct reduction of the oxides to vanadium metal was observed, and lithium oxide was present in the reaction mixture. The nitrogen content of the lithium was then increased, and the interaction of vanadium metal with the dissolved nitrogen studied. All reactions were carried out using an excess of liquid lithium, and this excess was removed, on completion of the reaction, by vacuum distillation at 600°. At the end of the distillation process the solid products of the initial reaction are present as an intimate mixture under vacuum conditions at 600°. At this temperature, solid lithium nitride will react with vanadium metal and will also decompose to lithium metal and nitrogen. To differentiate between reactions taking place during the distillation process and reactions in the presence of excess lithium, some products have also been extracted by solution of the excess of lithium in liquid ammonia.

EXPERIMENTAL

Purification of Lithium.—The lithium used in this work was of nominal 99·98% purity (Koch–Light) and supplied in the form of 3 × 2 cm ingots. The filtration unit consists of a stainless steel sinter plate welded into a stainless steel column (diam. 4·5 cm). A vacuum-tight screw-on top, fitted with an Edwards ¼ in. valve, gave access for filling the column with lithium ingots prior to the filtration procedure. The drain tube from the filter unit passed directly into an evacuable steel dry-box. The filter unit and dry-box were evacuated to 10^{-4} mmHg pressure, and subsequently filled with argon purified by passage over calcium turnings at 400°. The filter unit and drain tube were heated electrically; chromel–alumel thermocouples welded to the apparatus enabled the temperature of the filtration to be controlled. The molten lithium was forced through the sinter and into the dry-box by applying a positive argon pressure above the sinter, the rate of filtration being controlled by a valve fitted to a line passing from the top of the column to the drain tube below the sinter. Filtration of the lithium was always into small crucibles (3·7 cm long, 2·5 cm diameter) constructed from type 321 stainless steel. The crucibles were stored, after the lithium had cooled, in large stoppered glass tubes.

Procedure.—The oxide (*ca.* 1 g) was added to lithium (*ca.* 6 g) at 200° in an argon atmosphere. The oxide was added in small aliquots and was stirred into the metal using a stainless steel spatula. With V_2O_5, reaction was extremely exothermic and the oxide could only be added in very small quantities (0·02 g) at one time. Reaction of the lower oxides was progressively less vigorous. The mixture was cooled to room temperature, transferred to a sealed distillation vessel,[1] and allowed to equilibrate at 600° for 24 h. The excess lithium was then removed by vacuum distillation (10^{-4} mmHg) at 600°.

The Differential Thermal Analysis Apparatus.—The differential thermal analysis apparatus, used for the determination of reaction temperatures (Figure 1) was a development of the 0—400° apparatus used in the earlier sodium work.[6] The modifications required were an increase in the temperature range to 600° and adaptation to take account of the reactivity of lithium with glass. The lithium was contained in a steel vessel A (12 mm diam., 40 mm long) inside a silica glass tube B identical with that

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[1] C. C. Addison, M. G. Barker, R. M. Lintonbon, and R. J. Pulham, *J. Chem. Soc.* (*A*), 1969, 2457.

[2] C. C. Addison, M. G. Barker, and R. M. Lintonbon, *J. Chem. Soc.* (*A*), 1970, 1465.

[3] E. E. Hoffmann, U.S.A.E.C. Report ORNL 2674, 1959.

[4] P. I. Fedorov and M. T. Su, *J. Chinese Chem. Soc.*, 1957, **23**, 30.

[5] C. E. Messer, Chem. Soc. Special Publ. 22, 1967, p. 183.

[6] C. C. Addison and M. G. Barker, *J. Chem. Soc.*, 1965, 4483.

described earlier.[6] A steel tube C welded to the base of the steel vessel contained the chromel–alumel thermocouple, protected from electrical contact with the steel by silica sheathing. The furnace consisted of a mild steel block D (8 cm × 8 cm, 12 cm deep) drilled to accommodate the silica tubes and thermocouple wires. Four 250 W Solon heaters E enable temperatures of up to 800° to be attained. Furnace control was by a Ether controlled-heating-rate unit and it was found that a rate of 4 degrees per minute gave a satisfactory base line with liquid lithium as the reference material. Both reaction and reference samples were stirred throughout their liquid ranges by means of matched steel paddles driven through a belt mechanism from a variable speed electric motor. Two rubber o-rings on the drive shafts F gave free but guided running of the stirrer and provided a gas-tight seal. A positive pressure of argon was maintained over the samples throughout the heating and cooling cycles.

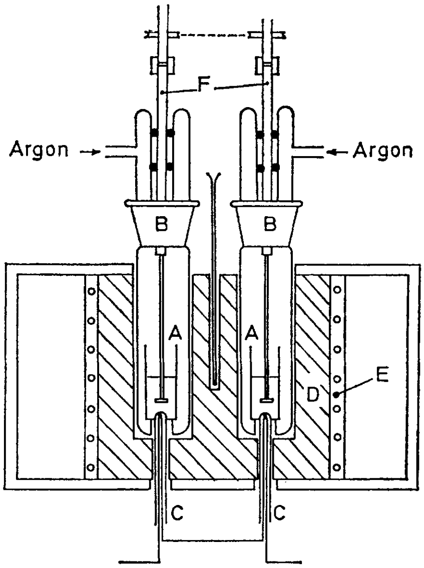

FIGURE 1 The differential thermal analysis apparatus

Preparation of Lower Oxides of Vanadium.—Vanadium sesquioxide, V_2O_3, was prepared by the hydrogen reduction of vanadium pentoxide at 600 °C for 3 h. Vanadium dioxide was prepared by heating a stoicheiometric mixture of the pentoxide and sesquioxide *in vacuo* at 700 °C for 48 h, and the monoxide by heating a stoicheiometric mixture of the pentoxide and vanadium metal at 1300 °C for 48 h. All the oxides were examined by *X*-ray powder diffraction and their patterns compared with published data.[7,8]

Analysis.—The products were normally examined by *X*-ray crystallography. However, a few analyses of the products were carried out to confirm that the reaction of vanadium pentoxide proceeds essentially in accordance with equation (1). After removal of the

$$V_2O_5 + 10Li \longrightarrow 5Li_2O + 2V \qquad (1)$$

excess of lithium by distillation, the product was extracted with water, and the aqueous extract titrated with hydrochloric acid using a pH meter [9] (Found: Li, 27·0; $5Li_2O + 2V$ requires 27·8%). For vanadium content, the product was extracted with ethanol, the residue dissolved in nitric acid, and vanadium determined by sulphur dioxide reduction followed by potentiometric titration with potassium permanganate.[9] The theoretical value from the above equation is V, 40·4%. In fact, the vanadium metal contains nitrogen, and a compound V_2N as product would require V, 38·4%. The vanadium content by analysis (estimated accuracy ±1%) varied from sample to sample, values ranging from the theoretical value (40·4%) to 36·5% were obtained; so that chemical analysis supports the above equation.

X-Ray Diffraction.—*X*-Ray diffraction patterns were recorded either with a Philips powder diffractometer or with a powder camera of diameter 14·83 cm. Samples were protected from attack by moisture and oxygen by loading, in an argon dry-box, into Lindemann glass capillaries which were sealed before loading into the camera. Diffractometer samples were loaded in the dry-box and were protected during exposure by a flow of dry nitrogen through the sample chamber. Both camera and diffractometer patterns were taken using Cu-K_α radiation.

RESULTS AND DISCUSSION

'Pure' Lithium.—Excess of nitrogen and oxygen were removed from liquid lithium by filtration at 250° through the stainless steel sinter. This method of purification reduces the oxygen and nitrogen contents of the lithium to not more than 0·01 and 0·04 wt. % respectively. These are the solubility values at 250°. All the vanadium oxides react with lithium at the melting point (179°). A typical differential thermal analysis trace (Figure 2) shows a small exothermic change (A) and a small endothermic change (B) which represent the melting of the lithium in the reference vessel and in the reaction vessel respectively. These changes arise because the quantities of lithium in the two vessels were not quite identical. The sharp exothermic change (C) denotes the reaction of the oxide V_2O_5 with

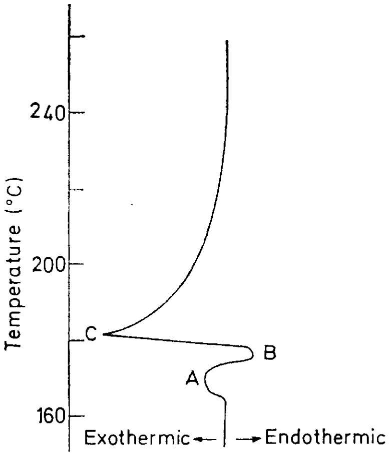

FIGURE 2 Differential thermal analysis of the liquid lithium–vanadium pentoxide reaction

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[7] G. Andersson, *Acta Chem. Scand.*, 1954, **8**, 1599.

[8] G. Andersson, *Research*, 1953, **6**, 455.

[9] A. I. Vogel, 'Quantitative Inorganic Analysis,' 3rd edn., Longmans, London, 1961, ch. 16.

the molten lithium in the reaction vessel. The lower oxides showed decreasing reactivity with lithium.

X-Ray powder diffraction patterns of products extracted from the excess of lithium by vacuum distillation corresponded with published data [10] for vanadium metal and lithium oxide only. An accurate determination of the lattice parameter of the vanadium metal produced in these reactions showed that lattice expansion had taken place. The value of the lattice parameter varied within the range $a = 3{\cdot}033$—$3{\cdot}038$ Å. The lattice parameter of pure vanadium [10] metal is $a = 3{\cdot}0231$ Å. The influence of dissolved nitrogen on the lattice parameter of vanadium metal has been measured recently by Henry *et al.*; [11] the α solid-solution range was found to extend to *ca.* 1·2 wt.% nitrogen at 600°. At this concentration the lattice parameter value is 3·043 Å. Above the saturation value two-phase behaviour was reported, the α phase co-existing with a hexagonal β phase. Since the narrow composition range of this β phase now [11] appears to lie between $VN_{0{\cdot}32}$ and $VN_{0{\cdot}36}$, it is convenient in this paper to refer to it as the V_3N phase. The presence of a very small quantity of the β phase was observed in the present work in those samples showing the greatest lattice expansion. Since the amount of data obtained at 600° by Henry *et al.* is somewhat limited, and the *X*-ray diffraction pattern of V_3N is diffuse and therefore difficult to observe, it is likely that at 600° the α solid-solution range is, in fact, less than 1·2 wt.% nitrogen.

Assuming that all the nitrogen in the liquid lithium is taken up by the vanadium metal, we have made rough estimates of the amount of nitrogen dissolved in the 'pure' lithium used in the reaction. The weight of vanadium metal produced in the reaction was known, and its nitrogen content could be calculated by using the lattice-parameter *vs.* nitrogen-content data.[11] As the approximate weight of lithium was also known it was possible to calculate the nitrogen content of the lithium used for the reaction. The results were in good agreement with the known solubility values (0·04 and 0·06 wt.% at 250 and 260° respectively). The results also indicate that the argon atmosphere used contained no nitrogen. The experiments described above were carried out in the steel evacuable dry-box into which the lithium was filtered. The argon in this box had been passed through the filter unit, and had thus been given extensive contact with liquid lithium at 250°.

Lithium containing Added Nitrogen.—Several reactions were carried out in a fibre-glass dry-box flushed with argon which had been previously dried by molecular sieve, and thus contained traces of nitrogen gas. Lithium readily extracts these traces from the argon atmosphere; the nitrogen content of the liquid lithium was thus increased, but was still well below the probable saturation value at 600°, the temperature at which the reaction products were heated in the liquid lithium. (No adequate data exists for the solubility of nitrogen in lithium at temperatures above 450°).

X-Ray diffraction patterns of products from these reactions corresponded with published data for the β phase V_3N,[12] together with the α solid-solution phase. For the formation of the α and β phases together, a mass-balance calculation indicates that the nitrogen content of the lithium must be between 0·1 and 0·8 wt.% N.

The β phase was extracted from the mixture ($Li_2O + V + V_3N$) by washing with ethanol followed by sulphuric acid. *X*-Ray powder diffraction patterns of the residue showed it to have the characteristic hexagonal close-packed structure with cell dimensions in good agreement with those given by Henry.[11] Samples prepared from liquid lithium containing traces of dissolved carbon as well as nitrogen showed a slight increase in the cell dimensions for V_3N, suggesting the formation of the carbo-nitride phase $\beta V_3(C,N)$. Brauer and Schnell [13] have shown that the presence of carbon in the β-nitride increases the cell constant by the same order as that observed in this study. Combustion analysis of this phase verified the presence of both carbon and nitrogen in the samples.

Further additions of nitrogen to the lithium resulted in products whose *X*-ray powder diffraction patterns corresponded to the β phase together with the body-centred cubic γ phase VN.[10] For the formation of these phases, mass-balance calculations indicate that nitrogen contents of between 0·9 and 1·7 wt.% nitrogen are required in the liquid lithium. At concentrations in excess of 2·6 wt.% nitrogen, lithium contains more nitrogen than is required for the complete formation of the nitride VN. To achieve these conditions, appropriate weights of solid lithium nitride were added. The products of reaction were the ternary nitride Li_7VN_4 together with the nitride VN, the former compound being identified by its powder *X*-ray diffraction pattern, which was identical to that given by Juza [14] for Li_7VN_4.

Reaction of Stoicheiometric Quantities.—The β-nitride V_3N has been found [11] to have an extremely narrow range of composition ($VN_{0{\cdot}32}$—$VN_{0{\cdot}36}$). To prepare this compound alone by the interaction of vanadium metal with nitrogen in liquid lithium it was necessary to add a stoicheiometric quantity of nitrogen gas to the lithium. The oxide VO was first added to an excess of the liquid lithium and then the required quantity of nitrogen gas added manometrically to the mixture:

$$Li + VO + N_2 \longrightarrow Li_2O + V_3N$$

The reaction was carried out at the relatively low temperature of 250°, the liquid metal being stirred magnetically throughout the duration of the experiment (3 days). The products, isolated by vacuum distillation were

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[10] Diffraction Data File, A.S.T.M., Philadelphia.

[11] J. L. Henry, S. A. O'Hare, R. A. McCune, and M. P. Krug, *J. Less Common Metals*, 1971, **25**, 39.

[12] H. Hahn, *Z. anorg. Chem.*, 1949, **258**, 58.

[13] G. Brauer and W. D. Schnell, *J. Less Common Metals*, 1964, **6**, 326.

[14] R. Juza, W. Gieren, and J. Haug, *Z. anorg. Chem.*, 1959, **300**, 61.

identified by X-ray powder diffraction as lithium oxide and the β-nitride V_3N.

Mechanism of Reaction.—There are two possible routes by which the vanadium nitrides may be formed in these reactions. Firstly, the vanadium metal may react with nitrogen dissolved in lithium, and remain unchanged during distillation of the lithium. Secondly, the reaction product after distillation of the lithium may contain vanadium metal and lithium nitride, which then react in the solid state *in vacuo* at 600°. The following observations support the first of these mechanisms.

(*a*) Lithium nitride begins to decompose at 538° *in vacuo*.[15] A series of solid-state reactions between lithium nitride and vanadium metal showed that only partial reaction took place at 550°. For example, the reaction of 1 mole of vanadium metal with 1 mole of lithium nitride at 550° gave V_3N as product, rather than the nitride VN.

(*b*) One of the experiments described above, employing a small quantity of nitrogen and producing the α solid-solution phase with some V_3N, was repeated, again at 200° with equilibration at 600°, and in the presence of an excess of lithium. Instead of distillation, the lithium metal was removed by solution in liquid ammonia, and products were found to be identical with those obtained by lithium distillation.

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[15] Handbook of Chemistry and Physics, 45th ed., The Chemical Rubber Co., Cleveland, Ohio, 1965.