Influence of Dissolved Nitrogen and Carbon on Reactions of Cerium(III) and Cerium(IV) Oxides with Liquid Lithium

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Cerium(IV) oxide, CeO_2, reacts with pure liquid lithium at 360 °C to give the previously unreported ternary oxide $LiCeO_2$. The latter is not stable towards nitrogen dissolved in the liquid metal. Reaction of both CeO_2 and cerium(III) oxide, Ce_2O_3, with liquid lithium containing dissolved nitrogen gives lithium oxide and cerium mononitride, CeN, as products. At higher nitrogen concentrations the formation of the ternary nitride Li_2CeN_2 has been observed. Reaction of CeO_2 with liquid lithium containing dissolved carbon gives Li_2O and the carbide CeC as products. Cerium(III) oxide does not react with pure liquid lithium.

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 and transition-metal oxides. The behaviour of transition-metal oxides in liquid lithium was shown [3] to differ from that in other alkali metals since lithium oxide has a free energy of formation much larger than many transition-metal oxides. The oxides of vanadium were shown to be reduced directly to the metal and Li_2O was observed in the reaction mixture. The free energies of formation of cerium(III) oxide, Ce_2O_3 [$-\Delta G_{298}$ 574.0 kJ (g-atom O)$^{-1}$], and cerium(IV) oxide, CeO_2 [$-\Delta G_{298}$ 514.2 kJ (g-atom O)$^{-1}$], are both close to that of Li_2O [$-\Delta G_{298}$ 560.65 kJ (g-atom O)$^{-1}$] and at 600 °C the values for Li_2O and CeO_2 are almost identical. From a purely thermodynamic standpoint it seems unlikely that CeO_2 will be reduced directly to cerium metal by liquid lithium since the reduction to Ce_2O_3 is more favourable. The oxide Ce_2O_3 should be stable to reduction by pure liquid lithium. By analogy with other alkali-metal systems, the formation of ternary oxides in these reactions, therefore, seems most likely, and it will be shown that CeO_2 reacts with pure liquid lithium to form the previously unreported ternary oxide $LiCeO_2$.

Lithium is unique amongst the alkali metals in that the solubilities of nitrogen,[4] carbon,[5] and hydrogen [6] are such that considerable quantities of these non-metals may be dissolved in it. Reactions may also be carried out between these non-metals and transition metals in liquid lithium,[3] since their free energies of formation are much lower than that of Li_2O. The influence of dissolved nitrogen and carbon on the reactions of the cerium oxides with liquid lithium will be described in this paper. It will be shown that the ternary oxide $LiCeO_2$ is not stable in the presence of dissolved nitrogen or carbon in liquid lithium. In the presence of appreciable quantities of dissolved nitrogen the reaction products are the nitrides CeN and Li_2CeN_2 together with Li_2O.

EXPERIMENTAL

A study of the purification of liquid lithium has shown [4] that the solubility of nitrogen is appreciable even at the m.p. of lithium. Lithium may not, therefore, be purified completely by a filtration method. In this study lithium was purified by heating the crude metal with a mixture of titanium (55), zirconium (35), and yttrium (10%) in sponge form. Pure lithium was then separated from the mixture by vacuum distillation at 600 °C and 10^{-4} mmHg.† Titanium and zirconium remove nitrogen by reaction to form solid nitrides and yttrium removes oxygen by formation of an oxide.

The methods employed for the reaction of oxides with liquid lithium have been described previously.[3]

RESULTS

Reaction of CeO_2 *with Pure Lithium and Lithium containing Nitrogen.*—Differential thermal analysis showed that cerium dioxide reacted with liquid lithium at 360 °C, the reaction being strongly exothermic; the nature of the reaction product was, however, influenced by the level of nitrogen impurity in the liquid lithium, and to a lesser extent by the temperature at which the excess of lithium was removed by vacuum distillation. The conditions used and identity of the reaction products are given in Table 1. With the nitrogen content at a negligible level the reaction of CeO_2 with liquid lithium gave the previously unreported compound $LiCeO_2$ (Found: Ce, 77.1; Li, 4.10. Calc. for $CeLiO_2$: Ce 78.2, Li, 3.90%). The *X*-ray powder diffrac-

TABLE 1

Reactions of cerium(IV) oxide with liquid lithium

Experiment no.	θ_c/°C		Impurity level */ atom % N	Products
	Equilibration	Distillation		
(1)	520	620	Pure Li	$LiCeO_2$
(2)	550	600	Pure Li	$LiCeO_2$
(3)	500	570	Pure Li	$LiCeO_2$ + an unknown phase
(4)	570	600	0.073 (1 : 0.3)	$LiCeO_2$ + CeN + Li_2O
(5)	590	600	0.146 (1 : 0.9)	CeN + Li_2O
(6)	570	620	0.254 (1 : 1.1)	CeN + Li_2O + trace Li_2CeN_2
(7)	550	570	0.243 (1 : 1.5)	Li_2O + CeN + Li_2CeN_2
(8)	570	600	0.498 (1 : 3.2)	Li_2CeN_2 + Li_2O + CeN
(9)	580	620	0.732 (1 : 4.2)	Li_2CeN_2 + Li_2O

* Ce : N Ratios are given in parentheses.

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† 1 mmHg ≈ 13.6 × 9.8 Pa.

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[3] C. C. Addison, M. G. Barker, and J. Bentham, *J.C.S. Dalton*, 1972, 1035.

[4] E. E. Hoffman, U.S.A.E.C. Report ORNL 2894, 1960.

[5] P. I. Federov and M. J. Su, *J. Chinese Chem. Soc.*, 1957, **23**, 30.

[6] C. E. Messer, *Chem. Soc. Special Publ.*, no. 22, 1967, p. 183.

tion pattern was found to be very similar to that reported [7] for the compound $LiPrO_2$ and was therefore indexed on the basis of a monoclinic unit cell, with $a = 5.82$, $b = 6.15$, $c = 5.77$ Å, and $\beta = 102° 27'$ (Table 2), to fall in the δ-$LiMO_2$ series of La, Pr, and Nd. In experiment (3) an unknown phase was observed together with the ternary oxide $LiCeO_2$. This phase was only observed when the excess of alkali metal was removed by distillation at temperatures below 600 °C. On reheating the mixture *in vacuo* at 640 °C lithium was evolved and *X*-ray diffraction showed only the compound $LiCeO_2$ to be present. The unknown phase could not be obtained as a pure product and its *X*-ray diffraction pattern (comprising some six lines with *d* values 6.90, 5.21, 3.32, 3.24, 2.77, and 2.71 Å, and intensities 100, 45, 25, 20, 12, and 11, respectively) could not be assigned to any known compound of lithium–cerium and oxygen.

TABLE 2

X-Ray diffraction pattern of $LiCeO_2$

			$\sin^2\theta$	
d/Å	I/I_0	*hkl*	obs.	calc.
5.662	14	100	0.0185	0.0184
4.154	52	(110), (011)	0.0345	(0.0341), (0.0344)
3.644	96	$\bar{1}11$	0.0448	0.0448
3.127	100	111	0.0608	0.0608
3.076	12	020	0.0628	0.0628
2.826	40	002	0.0744	0.0748
2.710	34	(120), (021)	0.0810	(0.0812), (0.0815)
2.541	97	($\bar{1}21$), (211)	0.0920	(0.0919), (0.0920)
2.332	9	102	0.1092	0.1092
2.254	3	$\bar{2}02$	0.1170	0.1164
2.180	13	112	0.1250	0.1249
2.120	8	$\bar{2}12$	0.1322	0.1321
2.080	19	022	0.1373	0.1376
2.064	23	($\bar{2}21$), ($\bar{1}22$)	0.1395	(0.1391), (0.1400)
1.929	25	(130), (031), ($\bar{3}01$)	0.1597	(0.1597), (0.1600), (0.1603)
1.893	9	300	0.1659	0.1656
1.862	16	($\bar{1}31$), (122)	0.1714	(0.1706), (0.1720)
1.814	11	(310), (202)	0.1806	(0.1803), (0.1804)
1.800	14	131	0.1867	0.1866
1.756	10	$\bar{3}02$	0.1928	0.1924
1.686	16	($\bar{3}12$), (301), ($\bar{2}13$)	0.2091	(0.2081), (0.2083), (0.2096)
1.661	8	230	0.2153	0.2149
1.626	44	(311), (123)	0.2248	(0.2240), (0.2255)
1.610	1	320	0.2291	0.2284
1.542	9	231	0.2499	0.2496
1.526	5	$\bar{3}22$	0.2551	0.2552
1.520	10	($\bar{2}33$), ($\bar{2}32$)	0.2573	(0.2567), (0.2577)
1.486	11	140	0.2692	0.2696
1.455	2	$\bar{1}41$	0.2806	0.2803
1.444	3	$\bar{1}04$	0.2850	0.2856
1.414	7	(141), ($\bar{4}11$)	0.2972	(0.2963), (0.2968)

At relatively low concentrations of nitrogen in liquid lithium [experiment (4)] the mononitride CeN and Li_2O were found in the products together with the ternary oxide $LiCeO_2$. With increasing nitrogen content the proportion of $LiCeO_2$ decreased until the product consisted solely of CeN and Li_2O [experiment (5)]. The cubic unit cell of the mononitride was satisfactorily indexed on the basis of a dimension $a = 5.029$ Å, in close agreement with the reported [8] value of 5.023 Å. When the nitrogen concentration of liquid lithium was increased to a level higher than that required for formation of CeN alone, a further phase was observed in the diffraction patterns of the products [experiments (6)—(9)]. This phase was identified as the ternary nitride Li_2CeN_2 by comparison with the *X*-ray powder-diffraction patterns obtained from solid-state reactions of Li_3N and CeN in an atmosphere of nitrogen.[9,10] With increasing nitrogen concentration the proportion of Li_2CeN_2 increased at the expense of CeN. The reaction of CeO_2 with liquid lithium containing dissolved nitrogen and a Ce : N ratio of 1 : 4.2 gave a product comprising solely of the ternary nitride Li_2CeN_2 and Li_2O.

It is, therefore, concluded that the ternary oxide $LiCeO_2$ may only be stable in pure liquid lithium. Traces of nitrogen will convert the compound $LiCeO_2$ to CeN or Li_2CeN_2 depending on the quantity of nitrogen available for reaction. Addition of $LiCeO_2$ to lithium containing dissolved nitrogen confirmed this conclusion.

Reactions of CeO_2 *with Liquid Lithium containing Dissolved Carbon.*—Cerium dioxide was treated with an excess of liquid lithium to which had been added various quantities of carbon in powder form. The products of reaction were identified by *X*-ray powder diffraction of the solid remaining after the excess of alkali metal had been removed by vacuum distillation. The results of the *X*-ray study are shown in Table 3. The stability of the compound $LiCeO_2$ towards dissolved carbon was found to be analogous to that observed with dissolved nitrogen. The monocarbide CeC was found in the products of all the reactions; however, the cubic sesquicarbide, Ce_2C_3, and the tetragonal dicarbide, CeC_2, were not observed. The monocarbide phase was indexed as a cubic unit cell with $a = 5.021$ Å in close agreement with the value determined by Dancy *et al.*[11] In experiments with a Ce : C ratio of 1 : 1 or 1 : 2 the products consisted solely of the carbide CeC and Li_2O. At higher carbon contents two further products were observed and the proportion of CeC to Li_2O decreased. The colours of the products from experiments (5) and (6) were red-brown and red respectively, indicative of cerium being present in the unknown phases in the oxidation state IV. Since no *X*-ray data are available for ternary lithium–cerium carbides these compounds could not be further characterised.

TABLE 3

Reactions of cerium(IV) oxide with liquid lithium containing dissolved carbon

	θ_c/°C			
Experiment no.	Equilibrium	Distillation	Carbon level */ atom %	Products
(1)	590	600	0.15 (1 : 0.5)	$LiCeO_2$ + CeC + Li_2O
(2)	590	600	0.31 (1 : 1)	CeC + Li_2O
(3)	650	590	0.30 (1 : 1)	CeC + Li_2O
(4)	650	590	0.56 (1 : 2)	CeC + Li_2O
(5)	650	590	1.11 (1 : 4)	CeC + Li_2O + one unknown phase
(6)	650	590	2.28 (1 : 8)	Li_2O + unknown phases + CeC

* Ce : C Ratios are given in parentheses.

Reaction of Cerium(III) *Oxide with Liquid Lithium.*—Cerium(III) oxide did not react with pure liquid lithium. The *X*-ray powder-diffraction pattern of the product at

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[7] N. I. Sevostyanova, I. A. Muraveva, L. M. Kovba, L. I. Martynenko, and V. I. Spitsyn, *Doklady Akad. Nauk S.S.S.R.*, 1965, **161**, 1359.

[8] G. V. Samsanov and M. D. Lyutaya, *Zhur. priklad. Khim.*, 1962, **35**, 2359.

[9] M. G. Barker and I. C. Alexander, *J.C.S. Dalton*, 1974, 2166.

[10] D. Halot and J. Flahaut, *Compt. rend.*, 1971, **272**, 465.

[11] E. A. Dancy, L. H. Everett, and C. L. McCabe, *Trans. Amer. Inst. Mining and Petroleum Engineers*, 1962, **224**, 1095.

600 °C showed only the diffraction lines of the starting oxide Ce_2O_3. However, in liquid lithium containing small quantities of dissolved nitrogen, the cubic mononitride, CeN, and Li_2O were produced together with some unchanged Ce_2O_3. At a Ce : N ratio of *ca.* 1 : 1 the product comprised only CeN and Li_2O, whilst at higher nitrogen levels the formation of the ternary nitride was again observed.

DISCUSSION

Thermodynamic arguments have already been used to show that Ce_2O_3 should not be reduced by liquid lithium; this conclusion has, therefore, been verified by the experimental evidence. From the experimental results an estimate of the free energy of formation of the ternary oxide, $LiCeO_2$, may be obtained. Since the compound is formed by reaction (1) at 600 °C, $-\Delta G_f^\ominus$ ($LiCeO_2$)

$$Li + CeO_2 \longrightarrow LiCeO_2 \qquad (1)$$

must be greater than $-\Delta G_f^\ominus$ (CeO_2). The compound is, however, less stable than a mixture of Li_2O and CeN since reaction (2) occurs. Therefore, from these observations, the free energy of formation of $LiCeO_2$ lies between

$$Li(N) + CeO_2 \longrightarrow 2Li_2O + CeN \qquad (2)$$

-917 kJ mol^{-1} [$\Delta G_f^\ominus$ (CeO_2)] and $-1\,173$ kJ mol^{-1} [$\Delta G_f^\ominus$ ($2Li_2O + CeN$)]. The thermodynamically most likely reduction of CeO_2 is to Ce_2O_3, but from experimental evidence the formation of $LiCeO_2$ must be more favourable. This implies that the lowest value for the free energy of formation of $LiCeO_2$ must be -996 kJ mol^{-1} obtained by adding the free-energy change for reaction (3) to the free energy of formation of CeO_2.

$$Li + 2CeO_2 \longrightarrow Ce_2O_3 + Li_2O \qquad (3)$$

Cerium(III) oxide does not form the ternary oxide $LiCeO_2$ in the presence of liquid lithium. Thus, from the reaction (4) it can be shown that 3 $\Delta G_f^\ominus$ ($LiCeO_2$) $<$ 2 $\Delta G_f^\ominus$ (Ce_2O_3), which gives a maximum value for the free energy of formation of $LiCeO_2$ as 1 022 kJ mol^{-1}.

$$Li + 2Ce_2O_3 \longrightarrow 3LiCeO_2 + Ce \qquad (4)$$

These arguments therefore give a final range for the free energy of formation of the ternary oxide, $LiCeO_2$, at 600 °C as between -996 and 1 022 kJ mol^{-1}.

Using similar arguments it may be shown that the oxides CeO_2, Ce_2O_3, and $LiCeO_2$ are thermodynamically unstable with respect to liquid lithium containing nitrogen and will therefore react with nitrogen in liquid lithium to form Li_2O and CeN. The oxides are unstable to dilute solutions of nitrogen in lithium; reaction (5),

$$Li + Li(N) + CeO_2 \longrightarrow 2Li_2O + CeN \qquad (5)$$

where Li(N) represents 1 p.p.m. nitrogen in liquid lithium, is favourable to the extent of -100 kJ mol^{-1}. Since the experiments were carried out in a static system, with a limited quantity of nitrogen available for reaction, the observed products were only seen to reach the stoicheiometry $2Li_2O + CeN$ when the Ce : N ratio was 1 : 1.

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