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MOLTEN LITHIUM CARBONATE–SODIUM CARBONATE–POTASSIUM CARBONATE EUTECTIC: THE REACTION OF GROUP VB AND VIB METAL OXIDES AND OXYANIONS

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ABSTRACT

The reactions of seven acidic oxides and oxyanions of Group VB and VIB metals with molten alkali metal carbonate eutectic have been studied by thermogravimetry. Products have been identified by reflectance, infrared and Raman spectroscopy and stoichiometries have been established for the sequential reactions as oxide anions were progressively incorporated, ultimately to form the ortho-oxyanion.

INTRODUCTION

At present, the chemistry of molten alkali metal carbonates is largely unknown, even though occasional measurements have been made in the course of other observations and often reported as a comparison with the behaviour of the same reactant in other melts. The more systematic investigations have been electrochemical and thus concerned with more dilute solutions. The major recent work has been carried out in the U.S. by Lorenz and Janz[1, 2] and in the U.S.S.R. by Smirnov and his school[3–9]. The earlier work was reviewed by Janz[10].

Carbonate melt chemistry has, however, been important for many years as such melts have been used, when containing dissolved cyanide, as baths for the carburizing of mild steel and to, a lesser extent, in preparative high temperature chemistry[11] as highly basic solvents when oxyanions of the less acidic transition metal oxidation states are required. A further use of potential importance is as the electrolyte of high temperature fuel cells.

However, in addition to such applications, molten carbonates have a definite interest in their own right as oxyanion melts of basic character. Thus a systematic investigation of their chemistry has been commenced and the reactions of the oxides and oxyanions in question compared, on the one hand, with the less basic and lower melting nitrates and higher melting sulphate melts, and, on the other hand, with the

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interaction of these acidic species with carbonate when both were dissolved in melts which acted as relatively inert solvents, in practice mainly in alkali metal chloride melts.

EXPERIMENTAL

Materials

Analar lithium carbonate, sodium carbonate and potassium carbonate (B.D.H.) were dried at 130° for 4 h, cooled in a desiccator, mixed in the eutectic ratio (32.1, 33.4, 34.5 wt.%, respectively) and melted, in small quantities, in a platinum crucible at 500°. The melt was kept under a carbon dioxide atmosphere for 5 h, allowed to solidify and ground finely in a dry box.

The acidic reagents of Analar [$K_2Cr_2O_7$, CrO_3 (B.D.H.)] and laboratory reagent grades [UO_3 (B.D.H.), WO_3, MoO_3, V_2O_5, $NaVO_3$ (Hopkins and Williams)] were all dried at 120° for 12 h.

Procedure

Reactions were carried out in 10 ml platinum or gold crucibles on a Stanton TR-1 thermobalance under a carbon dioxide atmosphere (flow rate 300 ml/min) using a heating rate of 2°/min. All reactants were "sandwich" mixed, a layer of powdered reactant being placed on a layer of melt and in turn covered with another layer of melt.

Infrared spectra were taken of powdered solidified reacted melts, pressed into thin discs with potassium bromide, on a Unicam SP200 or a Perkin-Elmer 225 spectrometer. Raman spectra were obtained from the powdered reacted melts with a Cary 82 instrument using an argon laser, and reflectance spectra on a Unicam SP800 or 1700 using the SP890 attachment.

RESULTS AND DISCUSSION

Potassium dichromate reacted with the carbonate at temperatures just below and just above the eutectic melting point, though this could have been somewhat lowered by solution of chromium compounds. Carbon dioxide was evolved and the melt itself contained chromate(VI) and was a bright yellow after quenching at the end of the reaction. Thermogravimetric analysis (Fig. 1, curve A) gave an average weight loss of 15.4% corresponding to the reaction

$$Cr_2O_7^{2-} + CO_3^{2-} \rightarrow 2\,CrO_4^{2-} + CO_2 \qquad (1)$$

which was analogous to that found for dichromate and carbonate in lithium chloride–potassium chloride eutectic at 400° (ref. 12) and in potassium nitrate at 350° (ref. 13). At higher temperatures, the same depolymerization reaction occurred without added carbonate, the oxide being supplied by the nitrate melt ($LiNO_3/KNO_3$ at 400°, $NaNO_3/KNO_3$ at 500° (ref. 14).

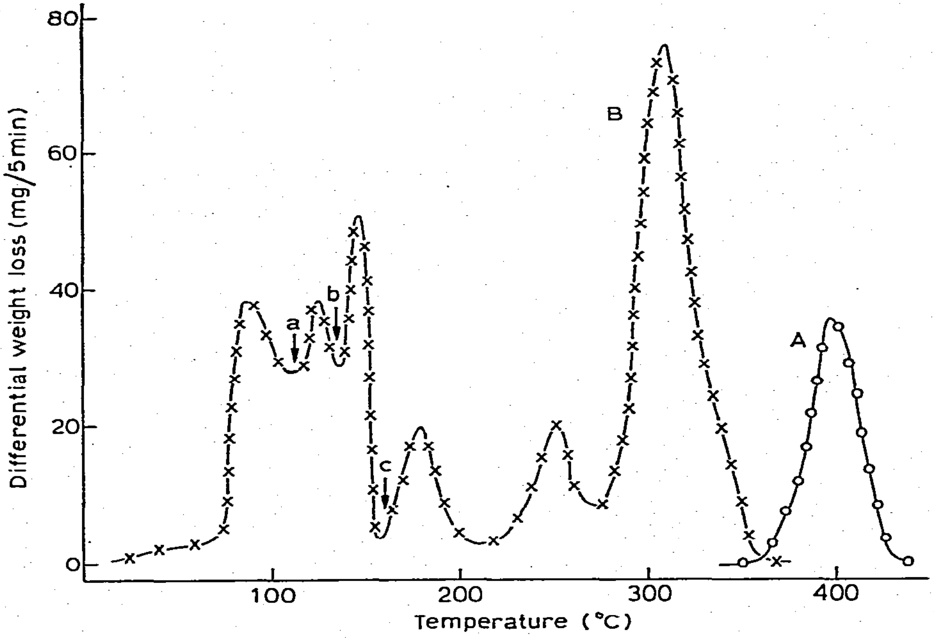

Fig. 1. Thermogravimetry of chromium compounds in lithium carbonate–sodium carbonate–potassium carbonate eutectic. Curve A, 0.97 m $K_2Cr_2O_7$; curve B, 2.5 m CrO_3.

Chromium(VI) oxide reacted with the carbonate eutectic almost entirely in the solid state (Fig. 1, curve B). Several maxima were apparent, the first minimum marked "a" corresponding to the formation of tetrachromate (average weight loss 10.9%)

$4\,CrO_3 + CO_3^{2-} \rightarrow Cr_4O_{13}^{2-}$ (2)
(Calc. weight loss 11.0%)

and the second "b" to trichromate with an average weight loss of 15.6%

$3\,CrO_3 + CO_3^{2-} \rightarrow Cr_3O_{10}^{2-}$ (3)
(Calc. weight loss 14.7%)

At both points, the cooled mixture was reddish-brown in colour with a rather similar vibrational spectrum (Table 1). The more major minimum marked "c" corresponded to the formation of dichromate with an average weight loss of 21.5%

$2\,CrO_3 + CO_3^{2-} \rightarrow Cr_2O_7^{2-} + CO_2$ (4)
(Calc. weight loss 22.0%)

when the solid mixture was a light brown. Further evolution of carbon dioxide occurred at somewhat higher temperatures, the average weight loss of 43.8% corresponding to the equation

$CrO_3 + CO_3^{2-} \rightarrow CrO_4^{2-}$ (5)
(Calc. weight loss 44.0%)

when the remaining solid was a bright yellow with a vibrational absorption more

TABLE 1

VIBRATIONAL SPECTRA OF PRODUCTS FROM REACTIONS WITH LITHIUM CARBONATE–SODIUM CARBONATE–POTASSIUM CARBONATE EUTECTIC

Reactant	*Maximum temperature (°C)*	*Reaction*	*Infrared*	*Raman*	*Ref.*
$K_2Cr_2O_7$	430	1	726 (m) 896 (w) 1080 (w)	354 (24) 854 (100) 868 (35) 879 (25) 908 (30)	28
CrO_3	120	2	775 (br. v.s.) 946 (br. s.)	315 (20) 857 (100) 931 (10) 1100 (18)	
CrO_3	140	3	678 (m) 762 (br. v.s.) 883 (s) 945 (br. v.s.)	352 (26) 855 (100) 931 (14) 1097 (30)	
CrO_3	160	4	801 (br. v.s.) 947 (s) 959 (s) 1000 (m)	347 (35) 856 (100) 930 (7) 1098 (28)	28, 29
CrO_3	360	5	726 (m) 896 (w) 1080 (w)	354 (24) 854 (100) 868 (35) 879 (25) 908 (24)	28
MoO_3	450		836 (v.br. vs) 906 (s) 1084 (s)	317 (92) 345 (34) 359 (21) 821 (35) 874 (35) 896 (100) 926 (18)	28, 30
WO_3	390		864 (m) 877 (m)	317 (89) 326 (100) 932 (84) 968 (59)	31
WO_3	440		854 (br. s.)	327 (100) 340 (36) 932 (98) 968 (20)	28, 30
UO_3	200		961 (v.br. s.)		20

TABLE 1 *(continued)*

Reactant	*Maximum temperature (°C)*	*Reaction*	*Infrared*	*Raman*	*Ref.*
UO_3	340		720 (w)		20
			880 (m)		
UO_3	470	6	720 (m)		20
			770 (w)		
			830 (s)		
$NaVO_3$	420	7	728 (w)	371 (28)	28, 31
			794 (br. w.)	818 (17)	
			924 (br. s.)	886 (100)	
			964 (s)	1076 (16)	
$NaVO_3$	560	9	730 (s)	369 (19)	28, 31
			769 (br. s.)	828 (19)	
				840 (24)	
			879 (br. v.s.)	853 (24)	
				889 (100)	
			1080 (br. m.)	1077 (26)	
V_2O_5	400	10	730 (m)	371 (38)	28, 31
			800 (br. s.)	790 (50)	
			862 (m)	820 (100)	
				844 (58)	
			927 (br. s.)	886 (80)	
			965 (m)	920 (49)	
				937 (54)	
V_2O_5	780	11	800 (br. v.s.)	349 (20)	28, 31
			890 (br. s.)	787 (36)	
				826 (100)	
				886 (23)	

characteristic of chromate(VI) (Table 1). Acid–base reaction of chromium(VI) oxide with carbonate has not been reported from chloride or nitrate melts, but the oxide was found to react stepwise with pure nitrate melts forming chromate, dichromate and possibly trichromate (in $LiNO_3/KNO_3$ at 600°, 400° and 132° (ref. 15), in $NaNO_3/KNO_3$ at 630°, 420° and 250° (ref. 14), and formed $Cr_2O_7^{2-}$ in KNO_3 at 350° (ref. 16).

Reflectance spectroscopy showed the final and penultimate products of the chromium(VI) oxide reactions to have spectra very like chromate and dichromate (Fig. 2, curves A and B), showing a steady shift of the maxima towards the ultraviolet as oxide anions are taken up.

Molybdenum(VI) oxide reacted at a higher temperature than chromium(VI) oxide, in fact, at the melting point of the eutectic (Fig. 3, curve A). The weight loss,

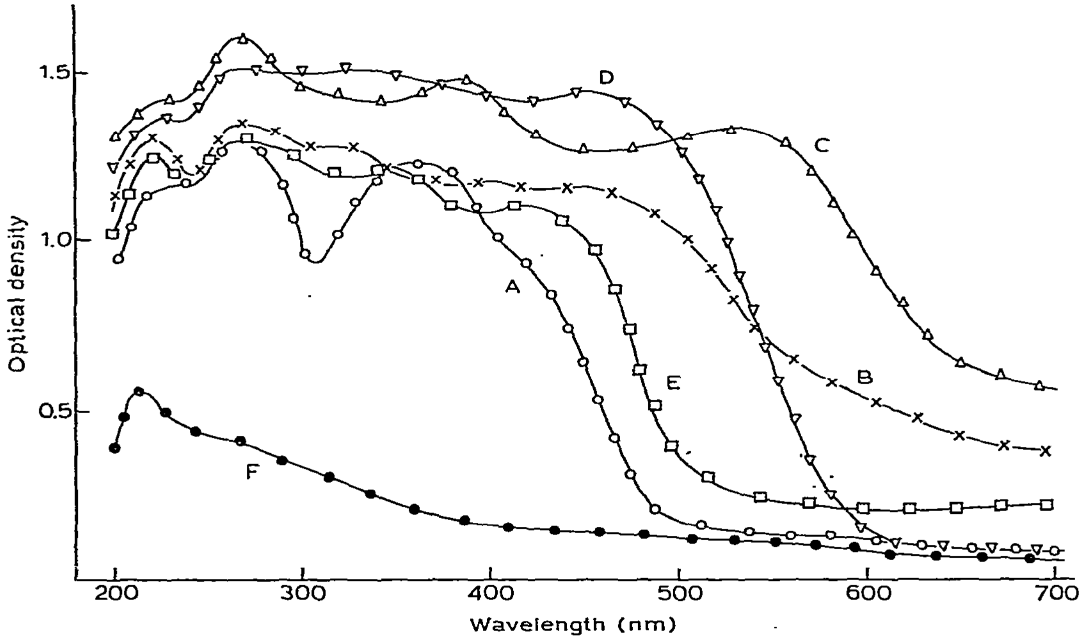

Fig. 2. Reflectance spectra of chromium compounds after reaction with melt. Curve A, CrO_3 in $Li_2CO_3/Na_2CO_3/K_2CrO_3$, final stage; curve B, CrO_3 in $Li_2CO_3/Na_2CO_3/K_2CrO_3$, third stage; curve C, CrO_3 alone; curve D, $K_2Cr_2O_7$ alone; curve E, K_2CrO_4 alone; curve F, melt alone.

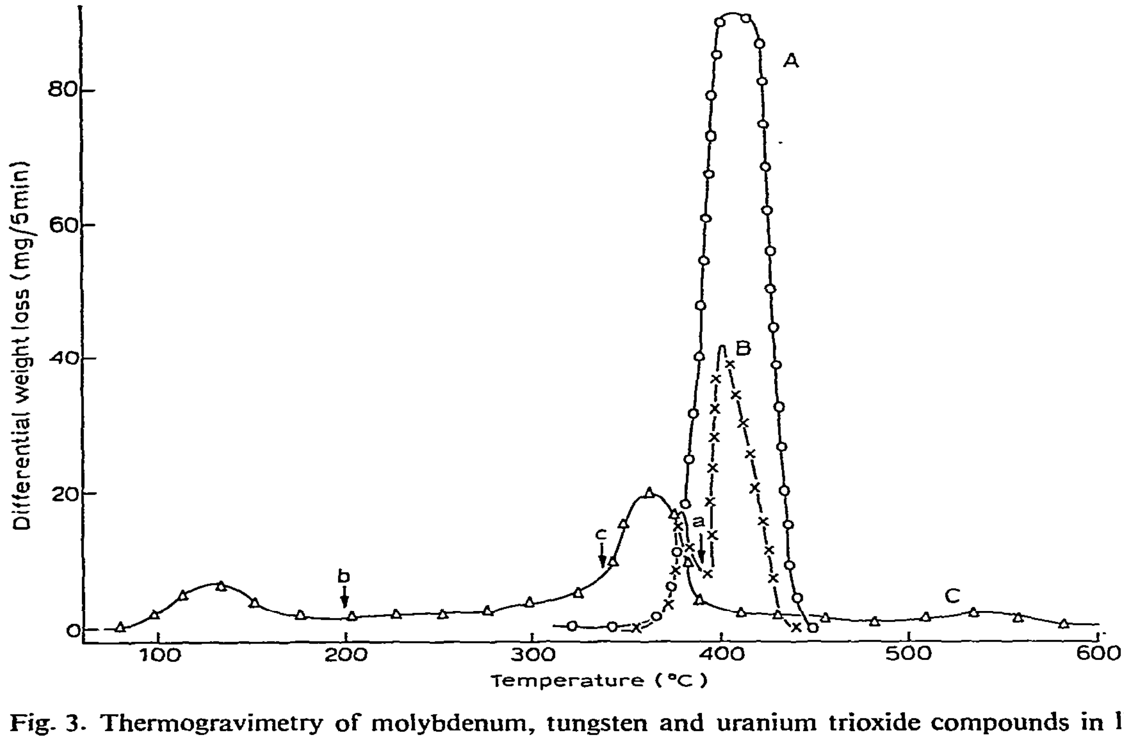

Fig. 3. Thermogravimetry of molybdenum, tungsten and uranium trioxide compounds in lithium carbonate–sodium carbonate–potassium carbonate eutectic. Curve A, 3.2 m MoO_3; curve B, 0.92 m WO_3; curve C, 1.8 m UO_3.

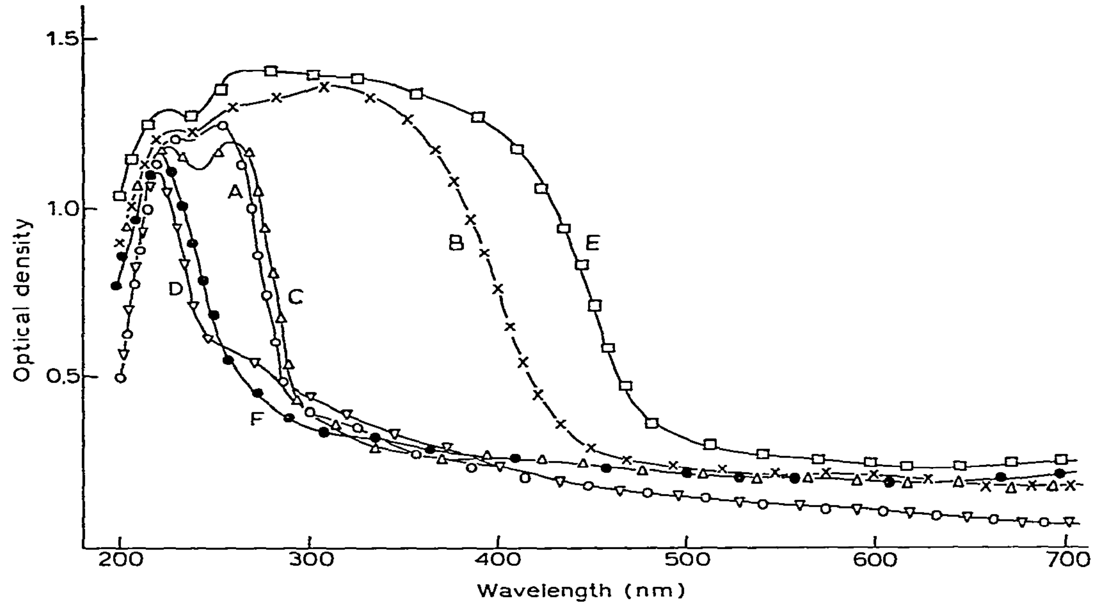

Fig. 4. Reflectance spectra of molybdenum and tungsten trioxide after reaction with melt. Curve A, ○, MoO_3 in $Li_2CO_3/Na_2CO_3/K_2CO_3$, final stage; curve B, ×, MoO_3 alone; curve C, △, $Na_2MoO_4 \cdot 2H_2O$ alone; curve D, ▽, WO_3 in $Li_2CO_3/Na_2CO_3/K_2CO_3$, final stage; curve E, □, WO_3 alone; curve F, ●, $Na_2WO_4 \cdot 2H_2O$ alone.

which averaged 30.8 %, corresponded closely to the analogue of reaction (5) for which the calculated weight loss was 30.6%. The creamy white solidified melt showed vibrational bands (Table 1) similar to those of orthomolybdate. The reflectance spectra from this solidified product showed a similar shift of the maxima to the ultraviolet with addition of oxide (Fig. 4, curves A and B) and the absorptions of the product to be very close to orthomolybdate (curve C).

Little information exists for this type of reaction in other melts except that, in nitrate melts, dissolved molybdenum(VI) oxide has been titrated with sodium carbonate to form orthomolybdate (in $NaNO_3/KNO_3$ at 330°)[17].

Tungsten(VI) oxide reacted at a slightly lower temperature, possibly showing a slightly more acidic nature than molybdenum(VI) analogous to their (anomalous) behaviour in aqueous solution.

The overall reaction (Fig. 3, curve B) gave an average weight loss of 19.5% corresponding to the analogue of reaction (5) which has a calculated loss of 19.0%. The white solidified melt produced showed several Raman and infrared bands of orthotungstate (Table 1) and its reflectance spectrum (Fig. 4, curve D) also gave similar bands (curve F). An intermediate minimum, marked "a", corresponded to an average loss of 7.5%, moderately close to the 9.5% calculated for the formation of ditungstate [cf. reaction (4)]. In other melts, more reactions have been reported than for molybdenum(VI) oxide. Thus tungsten(VI) oxide has been titrated potentiometrically with a 1 : 1 end point indicating orthotungstate in molten chloride[18] (as well as 2: 1 and 1 : 2 end points) and with sodium peroxide in molten potassium nitrate at 350° (ref. 16). The oxide has also been reported to react with molten rubidium and caesium carbonates at 950° (ref. 19).

Uranium(VI) oxide reacted with carbonate in the solid state from 80° (Fig. 3, curve C). The most prominent maximum rate of weight loss occurred probably a little below the melting point, but some slow reaction continued in the liquid state. The overall weight loss (average 18.8%) was close to the formation of orthouranate, i.e.

$$UO_3 + CO_3^{2-} \rightarrow UO_4^{2-} + CO_2 \quad (6)$$

(Calc. weight loss 15.4%)

The infrared absorptions of the orange-coloured quenched melt are given in Table 1. Whilst the reaction rate at lower temperatures did not vary as much as for chromium(VI) oxide, the position of the maxima was very consistent. The weight loss to the minimum after the first maximum at 130°, of 3.6–4.6%, marked "b" on the curve, was close to that expected for the formation of tetrauranate (calc. weight loss 3.85%) and the loss at the start of the second, larger, maximum marked "c", of 7.3–8.1%, was close to the formation of diuranate (calc. weight loss 7.7%). The greenish yellow and pale brown solids cooled from these temperatures had infrared absorptions characteristic of progressive addition of oxide[20].

The slow reaction of uranium(IV) oxide is characteristic since prolonged heating at 700–1000° was required for the formation of various uranate phases[20] (from mixtures of $UO_3 + Na_2CO_3$ of appropriate stoichiometries). Little work on the formation of uranates in other melts has been reported, but uranium(VI) oxide has been found to act as a Lux–Flood acid in molten nitrate to give an unspecified

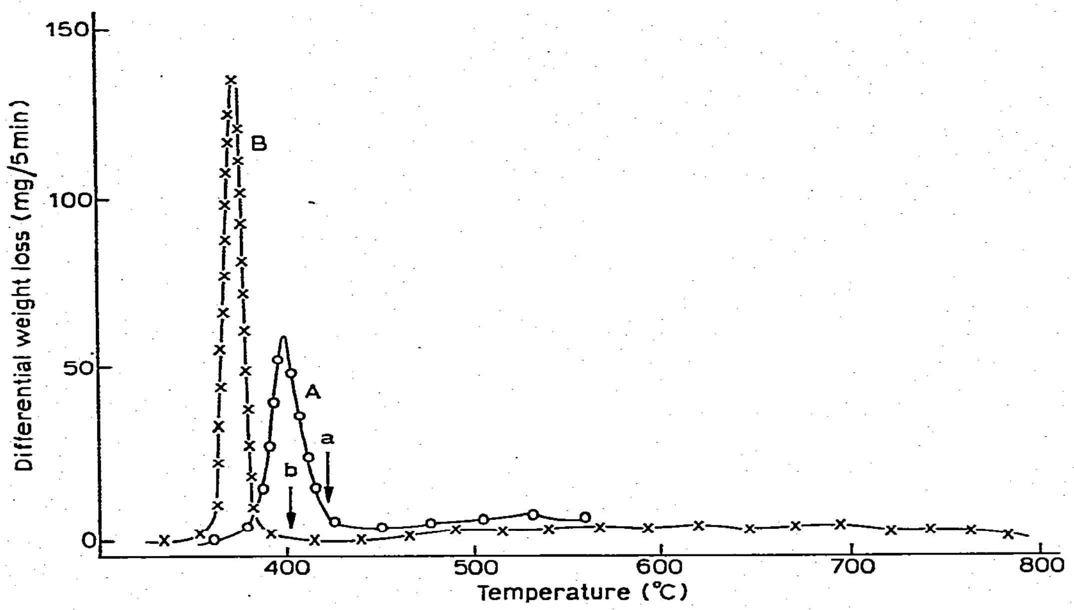

Fig. 5. Thermogravimetry of vanadium compounds in lithium carbonate–sodium carbonate–potassium carbonate eutectic. Curve A, 2.2 m $NaVO_3$; curve B, 0.83 m V_2O_5.

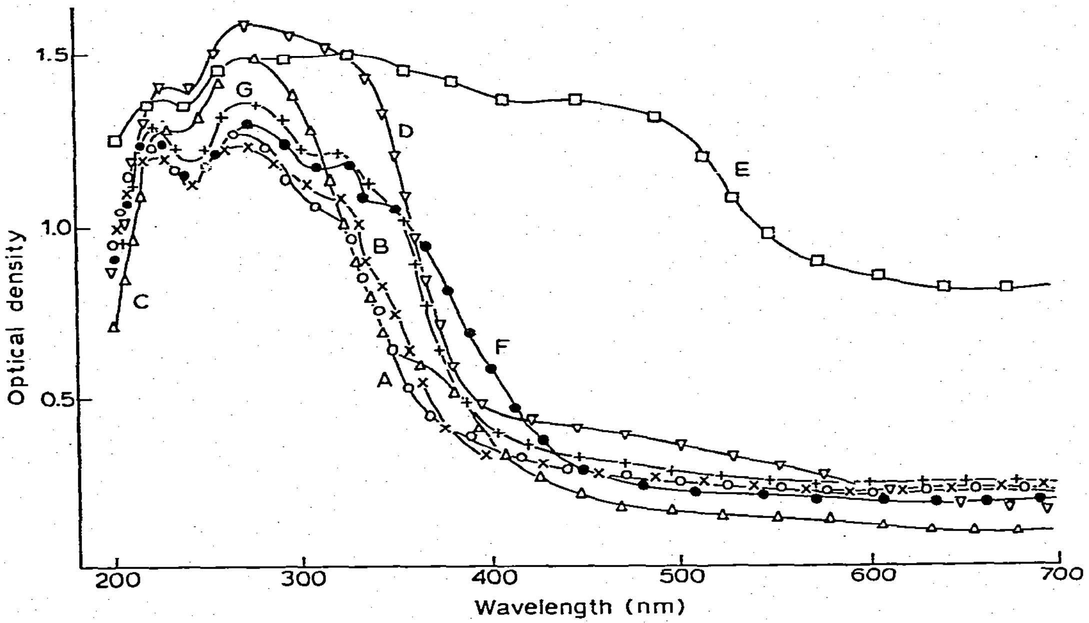

Fig. 6. Thermogravimetry of vanadium compounds in lithium carbonate–sodium carbonate–potassium carbonate eutectic. Curve A, ○, $NaVO_3$ in $Li_2CO_3/Na_2CO_3/K_2CO_3$, final stage; curve B, ×, $NaVO_3$ in $Li_2CO_3/Na_2CO_3/K_2CO_3$, first stage; curve C, △, V_2O_5 in $Li_2CO_3/Na_2CO_3/K_2CO_3$, final stage; curve D, ▽, V_2O_5 in $Li_2CO_3/Na_2CO_3/K_2CO_3$, first stage; curve E, □, V_2O_5 alone; curve F, ●, $NaVO_3$ alone; curve G, +, $Na_3VO_4 \cdot 14H_2O$ alone.

uranate[21] [and U_3O_8 in molten sodium sulphate to give $Na_2U_2O_7$ at 560–800° (ref. 22)].

Sodium metavanadate reacted with the ternary eutectic carbonate just below the melting point of the latter when pure, though the temperature may have been lowered by solution of vanadium compounds. Carbon dioxide was evolved, thermogravimetric analysis indicating a loss of 19.5% to 420° (marked "a" on Fig. 5, curve A) corresponding to the stoichiometry

$$2\,VO_3^- + CO_3^{2-} \rightarrow V_2O_7^{4-} + CO_2 \qquad (7)$$

(Calc. weight loss 18.1%)

After the reaction, the quenched melt was white and had vibrational absorption bands (Table 1) characteristic of pyrovanadate as well as metavanadate.

A further slow loss occurred with increasing temperature which shifts the equilibrium

$$CO_3^{2-} \rightleftharpoons O^{2-} + CO_2 \qquad (8)$$

to the right, and thus corresponds to increasing pH in the aqueous system when depolymerisation also occurs. In this case, orthovanadate was formed, as shown by the vibrational spectra of white quenched melt (Table 1) and the reflectance spectrum (Fig. 6, curve A). The weight loss to 560° was 30.6%.

$VO_3^- + CO_3^{2-} \rightarrow VO_4^{3-} + CO_2$ (9)
(Calc. weight loss 36.1%).

Similar reactions were found with vanadium(V) oxide (Fig. 5, curve B) the first reaction occurring at a slightly lower temperature, probably due to the higher acidity with a weight loss of 49.5% to 400° (marked "b")

$V_2O_5 + 2\,CO_3^{2-} \rightarrow V_2O_7^{4-} + 2\,CO_2$ (10)
(Calc. weight loss 48.4%)

followed by a slow loss to 800° of 69.1%, corresponding to the formation of orthovanadate (Table 1) as does the reflectance spectrum (Fig. 6, curve C)

$V_2O_5 + 3\,CO_3^{2-} \rightarrow 2\,VO_4^{3-} + 3\,CO_2$ (11)
(Calc. weight loss 72.6%)

In chloride melt solution, a similar overall reaction occurred, vanadium(V) oxide and carbonate reacting quantitatively to orthovanadate (in LiCl/KCl at 400°)[12], though metavanadate has also been reported[23].

The only previous reports of carbonate melts is that vanadium(V) oxide is soluble (1.8 mole % at 600°)[24] and hence probably reactive, and that acidity increases in the order "$KVO_3 < K_2O.4\,V_2O_5 < V_2O_5$" (ref. 25). However, in nitrate melts, vanadium(V) oxide was reported to react only slowly (in KNO_3 at 350°) to form metavanadate, which was a strong Lux–Flood acid and rapidly reacted to pyrovanadate, the latter reacting only slowly with nitrate (but faster with added sodium peroxide) to give orthovanadate as the final product[26]. Alternatively, in nitrate eutectics, reaction was progressive (at 280 and 410° in $LiNO_3/KNO_3$ and 320 and 400° in $NaNO_3/KNO_3$)[14] while in sulphate melts, acid–base reaction was complicated by reduction of a proportion of the vanadium to give vanadium bronzes[27].

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REFERENCES

1 P. K. Lorenz and G. J. Janz, *J. Electrochem. Soc.*, 116 (1969) 106.
2 P. K. Lorenz and G. J. Janz, *Electrochim. Acta*, 15 (1970) 1025, 2001.
3 T. I. Manukhina, I. N. Ozeryanaya and M. V. Smirnov, *Zashch. Met.*, 5 (1969) 228.
4 M. V. Smirnov, I. Y. Lyubimtseva and L. A. Tsvovkina, *Elektrokhimiya*, 7 (1971) 566.
5 N. Ozeryanaya, L. A. Tsvovkina and M. V. Smirnov, *Zashch. Met.*, 8 (1972) 128.
6 O. P. Penyagina, I. N. Ozeryanaya, M. V. Smirnov, B. S. Shibanov, and N. D. Shamanova, *Zashch. Met.*, 8 (1972) 312.
7 M. V. Smirnov, L. A. Tsvovkina and I. Y. Lyubimtseva, *Tr. Inst. Electrokhim. Ural. Nauchn. Tsentr Akad. Nauk SSSR*, 18 (1972) 122.

8 V. A. Oleinikova, L. A. Tsvovkina and M. V. Smirnov, *Tr. Inst. Electrokhim. Ural. Nauchn. Tsentr Akad. Nauk SSSR*, 19 (1973) 65.

9 I. N. Ozeryanaya, T. I. Manukhina and O. P. Penyagina, *Fiz. Khim. Electrokhim.*, 2 (1973) 94, 96.

10 G. J. Janz, *J. Chem. Educ.*, 44 (1967) 581.

11 M. G. Barker, *Inorganic Chemistry, Series One, M.T.P. International Review of Science*, Vol. 2, Butterworths/University Park Press, New York, 1972, Chap. 1.

12 J. D. Van Norman and R. A. Osteryoung, *Anal. Chem.*, 32 (1960) 398.

13 A. M. Shams El Din and A. A. El Hosary, *J. Electroanal. Chem.*, 17 (1968) 238.

14 D. A. Habboush and D. H. Kerridge, *Thermochim. Acta*, 60 (1974) 187.

15 B. J. Brough, D. H. Kerridge and S. A. Tariq, *Inorg. Chim. Acta*, 1 (1967) 267.

16 A. M. Shams El Din and A. A. El Hosary, *J. Electroanal. Chem.*, 9 (1965) 349.

17 J. M. Schlegel and R. Bauer, *Inorg. Chem.*, 11 (1972) 909.

18 V. I. Shapoval and V. F. Grischenko, *Ukr. Khim. Zh.*, 39 (1973) 867.

19 V. E. Plyushchev, V. M. Amosov and E. S. Razgon, *Izv. Akad. Nauk SSSR Neorg. Mater.*, 8 (1972) 1615.

20 E. H. P. Cordfunke and B. O. Loopstra, *J. Inorg. Nucl. Chem.*, 33 (1971) 2427.

21 C. J. Toussaint and A. Avogadro, *J. Inorg. Nucl. Chem.*, 36 (1974) 781.

22 V. K. Vaĭtsev, *Radiokhimiya*, 9 (1967) 733.

23 R. Molina, *Bull. Soc. Chim. Fr.*, (1961) 301.

24 V. V. Kuzmovich and N. K. Tumanova, *Elektrokhimiya*, 5 (1969) 1064.

25 A. Kato, F. Era, M. Nagano and J. Seiyama, *Kyushu Daigaku Kogaku Shuho*, 42 (1970) 939.

26 A. M. Shams El Din and A. A. El Hosary, *J. Electroanal. Chem.*, 7 (1970) 464.

27 A. Kato, K. Tomadu, I. Machida and T. Sekyama, *Bull. Soc. Chem. Jpn.*, 45 (1972) 690.

28 R. A. Nyquist and R. O. Kagel, *Infrared Spectra of Inorganic Compounds*, Academic Press, New York, 1971.

29 H. Stammreich, D. Bassi, O. Sala and H. Siebert, *Spectrochim. Acta*, 13 (1958) 192.

30 R. H. Bussey and O. L. Keller, *J. Chem. Phys.*, 41 (1964) 215.

31 W. P. Griffith and P. J. B. Lesniak, *J. Chem. Soc. A*, (1969) 1066.