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Note

THE REACTIONS OF POTASSIUM TETRACHROMATE IN THREE OXYANION MELTS

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The depolymerisation reactions of the polychromates have been studied in a number of oxyanion melts (i.e. $Cr_2O_7^{2-}$ in molten nitrate [1–3], nitrite [4] and carbonate [5], $Cr_3O_{10}^{2-}$ and CrO_3 in nitrate [2,3,6–8], nitrite [4] and carbonate [5]) and also in melts containing added base ($Cr_2O_7^{2-}$ in molten nitrates [9,10] and chlorides [11]).

The analogous reactions of tetrachromate were not examined, perhaps because of doubts arising from its method of preparation [12], that it might be a mixture of trichromate and chromium(VI) oxide. However, since the separate identity of tetrachromate has been confirmed by the publication of a crystal structure (indicating a zigzag linear chain) [13], the study of the corresponding depolymerisation reactions in oxyanion melts seemed desirable, both for their own sake and for the confirmation they might give to the structural studies.

EXPERIMENTAL

The three oxyanion melt eutectics were prepared as previously described [2,4,5]. Potassium tetrachromate was prepared by the method of Brauer [12] (found: K, 16.2; Cr, 39.7%; calc. for $K_2Cr_4O_{13}$: K, 15.8; Cr, 42.0%).

Thermogravimetric analysis was carried out on a Stanton TR-1 thermobalance, usually with a heating rate of 2°C min^{-1} on 2 g samples of well-ground and thoroughly mixed reactant and melt in 10-ml silica crucibles in the case of nitrate and nitrite melts, and gold crucibles with carbonate melt. The mass losses are reported as a percentage of the starting mass of the tetrachromate reactant, the average value and standard deviation for four determinations being given.

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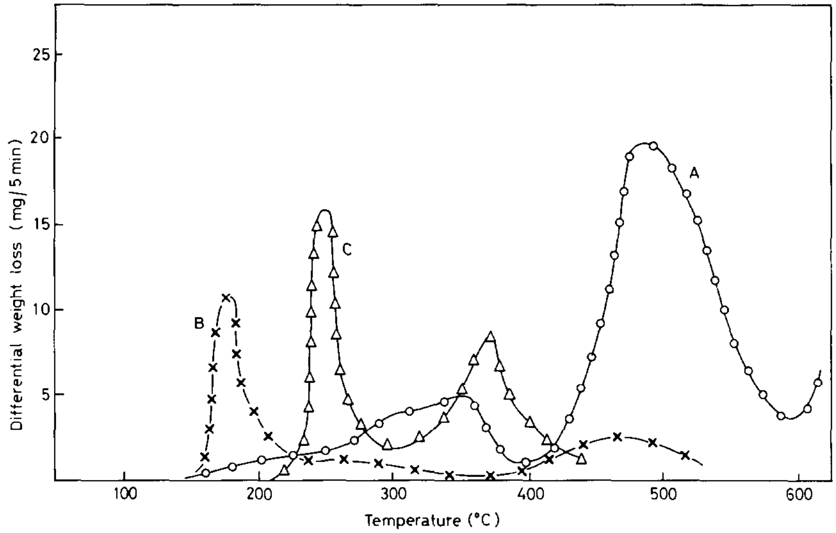

Fig. 1. TG curves of potassium tetrachromate in oxyanion melts. (A, ○) 0.46 *m* $K_2Cr_4O_{13}$ in $LiNO_3/KNO_3$ eutectic, (B, ×) 0.18 *m* $K_2Cr_4O_{13}$ in $NaNO_2/KNO_2$ eutectic, (C, △) 0.55 *m* $K_2Cr_4O_{13}$ in $Li_2CO_3/Na_2CO_3/K_2CO_3$ eutectic.

RESULTS AND DISCUSSION

Potassium tetrachromate reacted in all three melts forming chromate as the final product, the overall mass losses by thermogravimetric analysis being 64.4 ± 3.2% for $LiNO_3/KNO_3$ eutectic (sum of eqns. 1 and 3, 65.6%), 26.1 ± 1.5% for $Li_2CO_3/Na_2CO_3/K_2CO_3$ eutectic (sum of eqns. 2 and 4, 26.7%) and 46.1 ± 0.6% for $NaNO_2/KNO_2$ (eqn. 5, 46.1%). The frozen reacted melts dissolved in water yield yellow solutions (absorption maxima 26400 cm^{-1}) giving reactions for chromate.

However, both in molten nitrate and molten carbonate thermogravimetric analysis clearly showed two maxima (Fig. 1, curves A and C, respectively). The ratio of the first mass loss (to the minimum) to the second mass loss was 1 : 2.3 and 1 : 1.9, respectively, indicating the intermediate formation of dichromate in both cases, i.e.

$$K_2Cr_4O_{13} + 2NO_3^- \rightarrow 2Cr_2O_7^{2-} + 2K^+ + 2NO_2 + \tfrac{1}{2}O_2 \qquad (1)$$

(calc. mass loss for 2N + 5O = 21.9%)

$$K_2Cr_4O_{13} + CO_3^{2-} \rightarrow 2Cr_2O_7^{2-} + 2K^+ + CO_2 \qquad (2)$$

(calc. mass loss for CO_2 = 8.9%)

and

$$2Cr_2O_7^{2-} + 4NO_3^- \rightarrow 4CrO_4^{2-} + 4NO_2 + O_2 \qquad (3)$$

(calc. mass loss for 4N + 10O = 43.8%)

$$2Cr_2O_7^{2-} + 2CO_3^{2-} \rightarrow 4CrO_4^{2-} + 2CO_2 \qquad (4)$$

(calc. mass loss for $2CO_2$ = 17.8%)

even though the reaction with carbonate took place largely in the solid phase, as in fact did the reaction of chromium(VI) oxide with carbonate [5]. The temperatures at which the second mass loss commenced and at which it reached maximum rate of loss were also closely similar to those previously found for dichromate [2,5], though those for the first mass loss tended to be higher than those previously found for trichromate, indicating an irregular (or perhaps even a zigzag) relationship with increasing chromate chain length. In general, of course, as in other media, the reaction temperatures in a particular molten salt become lower as the degree of polymerisation increases. (No doubt largely due to the lower negative charge density of the larger chromate anions causing less repulsion to approaching basic (oxide/nitrate) anions, reaching the limit in the case of the highly reactive chromium(VI) oxide.) However, this charge density is not necessarily uniform along the chain, and in this case there appears to be preferential attack at the mid-point of the chain, which is also the point furthest from the presumably more highly charged terminal groups.

In molten nitrite, tetrachromate reacted completely in one stage (Fig. 1, curve B) at, or even below, the melting point of the eutectic

$$K_2Cr_4O_{13} + 6NO_2^- \rightarrow 4CrO_4^{2-} + 2K^+ + 3NO + 3NO_2 \qquad (5)$$

(calc. mass loss for 6N + 9O = 46.1%)

and provides a further example of the considerably greater basicity [14] and reactivity [4] of nitrite melts as compared to nitrate melts. This rapid, single-stage reaction blurs any differences in the depolymerisation reaction since potassium dichromate, trichromate and chromium(VI) oxide also have been found to react at similar temperatures [4].

In contrast the reaction in nitrate and carbonate melts does indicate a symmetrical splitting of the four-membered tetrachromate chain, rather than an end-clipping mechanism. Although data on comparable reactions in molten salts are as yet rare it may be noted that tetrametaphosphate (in $NaNO_3/KNO_3$) has been reported to form pyrophosphate in one stage whereas the trimetaphosphate adds on oxide stepwise [15].

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