MOLTEN LITHIUM NITRATE–POTASSIUM NITRATE EUTECTIC: THE REACTION OF RUTHENIUM(III), RHODIUM(III) AND PALLADIUM(II) CHLORIDES

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ABSTRACT

Ruthenium(III) chloride was oxidised in pure nitrate eutectic at 200–350 °C to dark blue ruthenium(IV) oxide, with some intermediate stabilisation due to formation of chloro-complexes. The oxide was initially somewhat amorphous but became fully crystalline after heating to 600 °C.

Rhodium(III) chloride dissolved to give yellow solutions, possibly involving nitrite coordination which gave brown insoluble potassium rhodate(III) ($KRhO_2$) from 300 °C. Additions of potassium chloride gave red solutions, and the increased chloro-complexation resulted in greater stability towards the Lux–Flood acid–base reaction.

Palladium(II) chloride also dissolved to give yellow solutions at 200 °C which reacted above 300 °C. Red solutions of chloro-complexes, formed on addition of potassium chloride, also showed increased stability with respect to that in pure nitrate, reacting only from 400 °C. In each case the dark brown insoluble product was palladium(II) oxide. The red chloride-containing melts had higher absorbances at 28 300 and 22 500 cm^{-1} than pure nitrate melts, indicating the formation of mixed chloro-nitrate complexes, probably octahedral, in the former.

INTRODUCTION

The reactions of compounds of platinum group metals in molten alkali metal nitrates have been studied very little. Indeed, no reports at all appear to have been published on palladium, while in the case of ruthenium there is only the old claim that the metal forms ruthenate(VI) on "fusion" with a mixture of potassium nitrate and potassium hydroxide [1].

With rhodium, the metal, used as a cathode in molten potassium nitrate at 350 °C, was reported to have reacted with reduction products of the nitrate to give "a yellow–brown solution which turned green on agitation", which was claimed as formation of rhodium(III) [2]. There is also a more extended study of rhodium(III) chloride in molten sodium nitrate–potassium nitrate eutectic, in which yellow solutions slowly formed (absorption maximum 28 200 cm^{-1}, $\epsilon = 2100$ l mol^{-1} cm^{-1}), which reacted to give black

precipitates of rhodium(III) oxide [3]. Dissolution was more rapid in melts containing added sodium nitrite, and the absorption spectrum became close to that of the dissolved hexanitro-complex $[K_3Rh(NO_2)_6]$. Alternatively, additions of potassium chloride formed a rose-coloured solution and caused a more marked change in the absorption (the maximum at 28 200 cm^{-1} diminishing, with new maxima appearing at 24 000 and 18 800 cm^{-1}), attributed to the octahedral hexachloro-complex $[RhCl_6]^{3-}$ found in molten lithium chloride–potassium chloride eutectic [3].

In order to extend this meagre information, comparable thermogravimetric and spectroscopic studies of the three chlorides were carried out in molten lithium nitrate–potassium nitrate eutectic.

EXPERIMENTAL

Materials

Potassium nitrate (AR, BDH) and lithium nitrate (reagent grade, BDH) were dried at 150°C for 24 h, mixed to eutectic composition (43 mol% $LiNO_3$), evacuated to 0.01 Torr over 10 h and filtered at 180°C through a No. 4 grade glass sinter in an oven. After solidification, the eutectic was broken up and stored in a dry box (P_2O_5 drying agent).

Ruthenium(III) chloride, rhodium(III) chloride and palladium(II) chloride (all Johnson–Matthey Chemicals) were used as received (Found: Ru 41.8, Cl 43.8%; calc. for $RuCl_3 \cdot 3H_2O$: Ru 38.6, Cl 40.7%. Found: Rh 40.5, Cl 41.4%; calc for $RhCl_3 \cdot 3H_2O$: Rh 39.1, Cl 40.1%. Found: Pd 59.6, Cl 39.5%; calc for $PdCl_2$: Pd 60.0, Cl 39.9%, respectively). Sodium hydroxide and potassium chloride (both AR, BDH) were dried at 100°C (4 h) and 150° (2 h) respectively.

Procedure

Qualitative reactions were carried out in Pyrex tubes closed with a silica gel drying tube and heated in an electric furnace fitted with an Ether Transitrol (Type 1291 B) temperature controller.

Thermogravimetry was carried out using a Stanton TR-1 thermobalance at a heating rate of 2° min^{-1}. The finely ground reactants and eutectic (3 g) were well mixed and contained in 10 ml silica crucibles. Weight losses are quoted as a percentage of reactant weight, and presented graphically as differential weight loss/temperature plots (hatched lines indicate isothermal conditions; when 2° equals 1 minute).

Analyses of reaction products were carried out by conventional qualitative and quantitative methods.

X-ray powder diffraction was carried out on a Philips (Eindhoven) diffractometer using nickel filtered copper $K\alpha$ radiation, the d spacings and intensities (listed in full in Ref. 4) being matched with those of known compounds listed in the JCPDS Index.

Electronic absorption spectra were obtained with a Unicam SP-700 spectrophotometer modified with reversed optics from 4000–13 000 cm^{-1} and with RF-heated cells.

RESULTS AND DISCUSSION

Ruthenium(III) chloride

Ruthenium(III) chloride ($RuCl_3 \cdot 3H_2O$) in lithium nitrate–potassium nitrate eutectic evolved nitrogen dioxide from 200–350°C (Fig. 1, curve B) with a weight loss of 82.6%; the smaller loss from 100–180°C of 6.7% consisted of an acid gas ($HCl/HNO_3/H_2O$) formed by partial hydrolysis. The final product was insoluble dark blue ruthenium(IV) oxide, that from heating to 400°C being imperfectly crystalline, but giving all the expected diffraction lines of the crystalline oxide after heating in the melt to 600°C.

$$RuCl_3 \cdot 3H_2O + 3NO_3^- \rightarrow RuO_2 + 3Cl^- + 3NO_2 + \tfrac{1}{2}O_2 + 3H_2O \qquad (1)$$
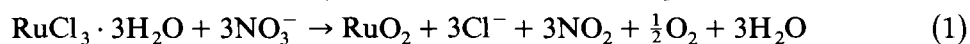
$$\left(\text{Calc. for loss of } 3NO_2 + \tfrac{1}{2}O_2 + 3H_2O \text{ per } RuCl_3 \cdot 3H_2O = 79.2\%\right)$$

The double maximum of curve B probably indicated some stabilisation due to chloro-complex formation, as has previously been found for iron(III) [5], cobalt(II) [6] and cerium(III) [7] in nitrate melts.
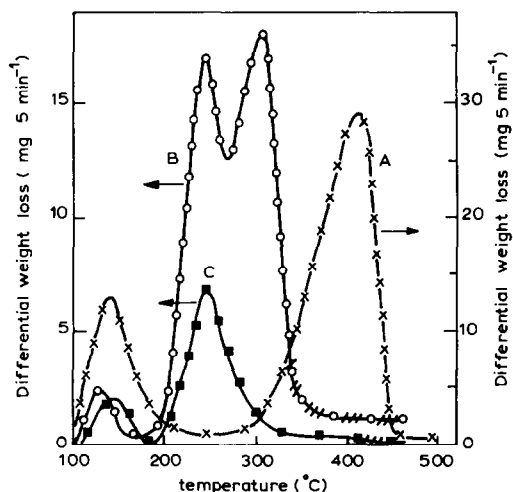

Fig. 1. Thermogravimetry of ruthenium(III) chloride. Curve A (– × –) $RuCl_3 \cdot 3H_2O$ (0.55 g) alone in air; B (–○–) $RuCl_3 \cdot 3H_2O$ (0.21 m) in $LiNO_3$–KNO_3 eutectic; C (–■–) $RuCl_3 \cdot 3H_2O$ (0.16 m) + NaOH (0.62 m) in $LiNO_3$–KNO_3 eutectic.

Similar products were obtained when the hydrated chloride was heated in air (Fig. 1, curve A) but the temperatures of reaction were higher, indicating the more ready availability of oxide ions in the melt; the overall weight loss of 47.2% was close to that for the hydrolysis/oxidation reaction

$$2RuCl_3 \cdot 3H_2O + \tfrac{1}{2}O_2 \rightarrow 2RuO_2 + 6HCl + 3H_2O \tag{2}$$

$\left(\text{Calc. for loss of } 3HCl + \tfrac{3}{2}H_2O\right.$

and gain of $\tfrac{1}{4}O_2$ per $RuCl_3 \cdot 3H_2O = 49.1\%\left.\right)$

Even lower reaction temperatures were observed with a nitrate melt containing added sodium hydroxide (Fig. 1, curve C; $RuCl_3$: NaOH ratio = 1 : 4) owing to the higher basicity of this melt solution. The dark blue precipitate from reaction at 400 °C was again shown to be ruthenium(IV) oxide by powder diffraction, and the quenched melt was found to contain nitrite. The overall weight loss of 34.6%, rather higher than for the postulated reaction

$$2RuCl_3 \cdot 3H_2O + 6NaOH + NO_3^- \rightarrow 2RuO_2 + 6NaCl + NO_2^- + 9H_2O \tag{3}$$
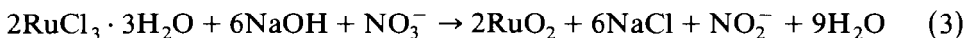
$\left(\text{Calc. for loss of } \tfrac{9}{2}H_2O \text{ per } RuCl_3 \cdot 3H_2O = 31.0\%\right)$

was considered to be in part due to a small amount of yellow–orange chlorine-containing sublimate from 120 °C (probably Ru_2OCl_4 or Ru_2OCl_6).

A similar reaction was observed when lithium hydroxide ($RuCl_3$: LiOH ratio = 1 : 2) was used, although X-ray diffraction also indicated the formation of a minor proportion of lithium ruthenate(IV) with the ruthenium(IV) oxide. However, when larger ratios of sodium hydroxide were used (1 : 16 and 1 : 26) and reacted at 450 °C for 2 h, the quenched melt, when dissolved in water, gave the dark blue precipitate with the d values of ruthenium(IV) oxide together with a yellow–orange aqueous solution with absorption maxima at 27 000 and 21 500 cm^{-1}, characteristic of ruthenate(VI) solutions [8–11], probably by a reaction such as

$$RuO_2 + 2OH^- + NO_3^- \rightarrow RuO_4^{2-} + NO_2^- + H_2O \tag{4}$$

Analogous formation of high oxidation states has also been reported in basic nitrate melts with neptunium {Np(VII) was formed in $NaNO_3$–KNO_3 eutectic by BrO_3^- when NaOH (7.5 m) was present; in neutral melts, neptunyl(V) only forms dineptunate(VI) [12,13]}. Similarly, manganate(VI) and manganate(V) were stabilised in nitrate melts containing sodium hydroxide [14] (in neutral melts manganate(VI) was formed).

Rhodium(III) chloride

Rhodium(III) chloride ($RhCl_3 \cdot 3H_2O$ dissolved in nitrate eutectic at 200 °C to give a yellow solution, which changed to red at 250 °C when nitrogen dioxide began to evolve. A dark brown precipitate formed above

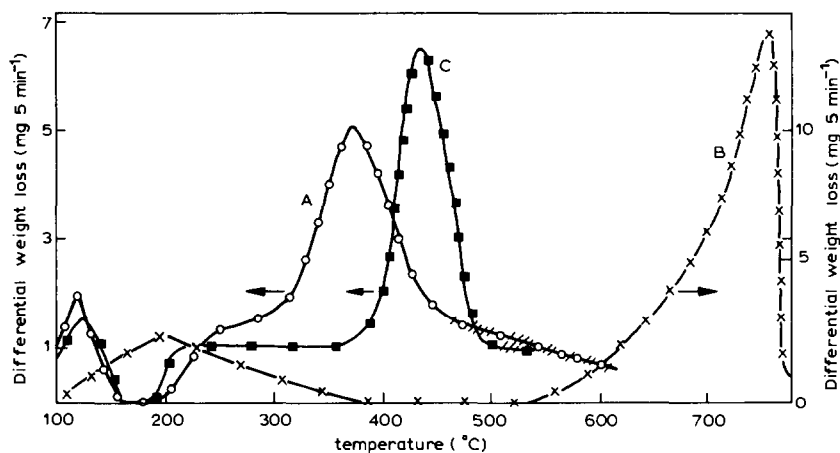Fig. 2. Thermogravimetry of rhodium(III) chloride. Curve A ($-\times-$) RhCl$_3 \cdot$3H$_2$O (0.06 m) in LiNO$_3$–KNO$_3$ eutectic; B ($-\circ-$) RhCl$_3 \cdot$3H$_2$O (0.29 g) alone in air; C ($-\blacksquare-$) RhCl$_3 \cdot$3H$_2$O (0.07 m) + KCl (0.73 m) in LiNO$_3$–KNO$_3$ eutectic.

300°C, which after extraction with water contained potassium but no lithium and gave the most intense diffraction line of rhodium(III) oxide (found: Rh 57.6%; calc. for KRhO$_2$: Rh 59.2%). After heating at 940°C for 4 h there was an 18.5% weight loss, and the product showed all the diffraction lines of the hexagonal form of rhodium(III) oxide [15], suggesting that the initial brown precipitate was a mixture of potassium rhodate(III) and rhodium(III) oxide {rather than entirely rhodium(III) oxide [3]}, and that on heating potassium oxide was volatilised

$$2KRhO_2 \rightarrow Rh_2O_3 + K_2O \tag{5}$$

$\left(\text{Calc. for loss of K} + \tfrac{1}{2}\text{O per KRhO}_2 = 27.0\% \right)$

Thermogravimetric analysis (Fig. 2, curve A) showed a first weight loss from 70–160°C (largely water) and a second from 200°C. The overall weight loss of 156.8% is higher than predicted from eqn. (6)

$$2RhCl_3 \cdot 3H_2O + 6NO_3^- \rightarrow Rh_2O_3 + 6Cl^- + \tfrac{3}{2}O_2 + 6H_2O + 6NO_2 \tag{6}$$

$\left(\text{Calc. for loss of 3H}_2\text{O} + 3\text{NO}_2 + \tfrac{3}{4}\text{O}_2 \text{ per RhCl}_3 \cdot 3\text{H}_2\text{O} = 82.0\% \right)$

probably due to melt decomposition (while held isothermally at 450°C for 5 h) catalysed by chloride anions [16]. Certainly, hydrated rhodium(III) chloride heated alone (Fig. 2, curve B) also showed two peaks, the overall weight loss of 48.6% being a little lower than predicted from eqn. (7)

$$2RhCl_3 \cdot 3H_2O + \tfrac{3}{2}O_2 \rightarrow Rh_2O_3 + 3Cl_2 + 6H_2O \tag{7}$$
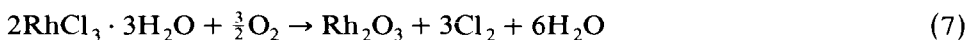
$\left(\text{Calc. for loss of 3H}_2\text{O} + \tfrac{3}{2}\text{Cl}_2 \text{ and gain of} \tfrac{3}{4}\text{O}_2 \text{ per RhCl}_3 \cdot 3\text{H}_2\text{O} = 51.8\% \right)$

In a nitrate melt containing dissolved potassium chloride (RhCl$_3$: KCl = 1 : 11) a red solution was formed at 200°C, which reacted similarly (Fig. 2,

curve C), the overall weight loss (166.7%) being larger still because the reacting melt was held at 470°C for 6 h. Stabilisation of rhodium(III) by chloride anions caused the maximum of the second reaction to occur some 60°C higher than in the absence of chloride, but both melts supplied oxide anions more readily than did air oxidation (Fig. 2, curve B).

The yellow solution formed from hydrated rhodium trichloride at 200°C showed an absorption maximum ($27\,500$ cm^{-1}, $\epsilon = 3400$ l mol^{-1} cm^{-1}) in a similar position to that found in sodium nitrate–potassium nitrate eutectic [$28\,000$ cm^{-1}, attributed to Rh(NO$_2$)$_6^{3-}$ species] [3], though the latter solvent showed a lower molar extinction coefficient. On addition of potassium nitrite to the yellow solution, the intensity increased a little, though with an absorption maximum ($27\,500$ cm^{-1}, $\epsilon = 3600$ l mol^{-1} cm^{-1}) similar to that found previously with the other eutectic, while the red solution formed by addition of potassium chloride (ratio RhCl$_3$: KCl = 1 : 310) had a much lower absorption coefficient with a similar maximum ($27\,500$ cm^{-1}, $\epsilon = 1600$ l mol^{-1} cm^{-1}). The further maxima found in sodium nitrate–potassium nitrate eutectic with higher ratios of chloride (e.g. 1 : 600) [3] were not apparent, although the $28\,200$ cm^{-1} band was reported to diminish with increasing chloride concentration [attributed to change from Rh(NO$_2$)$_6^{3-}$ anions to RhCl$_6^{3-}$].

Palladium(II) chloride

Palladium(II) chloride dissolved in the nitrate eutectic to give a yellow solution at 200°C; the colour darkened to red at 300°C, when a brown suspension began to form and nitrogen dioxide was evolved. After 3 h at 450°C, quenching and aqueous extraction, the dark brown insoluble powder gave the X-ray diffraction lines of palladium(II) oxide (found: Pd 85.5; calc for PdO; Pd 86.9%). The overall weight loss was 62.3% (Fig. 3, curve A), including 1 h isothermally at 450°C, which supported the reaction

$$PdCl_2 + 2NO_3^- \rightarrow PdO + 2Cl^- + 2NO_2 + \tfrac{1}{2}O_2 \tag{8}$$
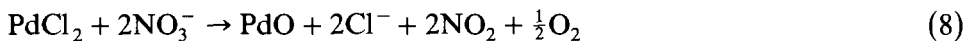
(Calc. for loss of 2 N + 5 O per PdCl$_2$ = 60.9%)

A metallic mirror of palladium on the glass surface indicated a small amount of reduction.

A similar but less easy reaction occurred when the palladium(II) chloride was heated in air (Fig. 3, curve B). Here the first weight loss (400–715°C) of 30.8% gave a black product with the d values of palladium(II) oxide (found: Pd 85.8; calc. for PdO: Pd 86.9%), i.e.

$$PdCl_2 + \tfrac{1}{2}O_2 \rightarrow PdO + Cl_2 \tag{9}$$

(Calc. for loss of Cl$_2$ and gain of $\tfrac{1}{2}$O$_2$ per PdCl$_2$ = 31.0%)

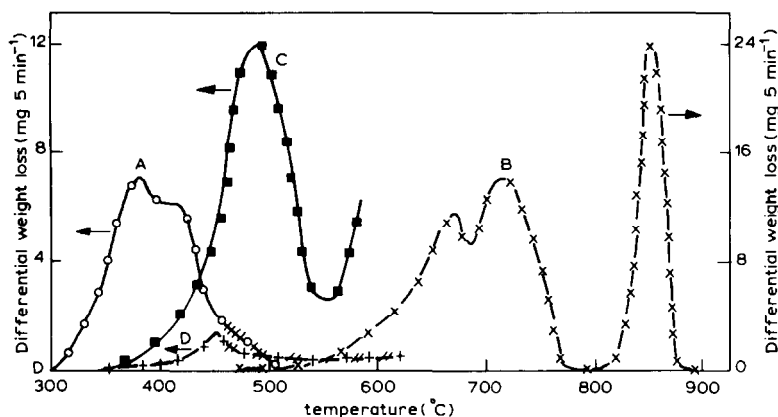(Simple comparison of free enthalpy of formation values would suggest that

Fig. 3. Thermogravimetry of palladium(II) chloride. Curve A $(-\circ-)$ $PdCl_2$ (0.11 m) in $LiNO_3-KNO_3$ eutectic; B $(-\times-)$ $PdCl_2$ (0.42 g) alone in air; C $(-\blacksquare-)$ $PdCl_2$ (0.22 m) + KCl (0.90 m) in $LiNO_3-KNO_3$ eutectic; D $(-+-)$ $PdCl_2$ (0.26 m) + KCl (3.0 m) in $LiNO_3-KNO_3$ eutectic.

the equilibrium lies well to the left, but it is in fact completely displaced to the right, no doubt because of removal of chlorine by the flow of air).

The product after the second weight loss (800–970 °C) of 8.9% had the lines of palladium metal (found: Pd 98.5%)

$$PdO \rightarrow Pd + \tfrac{1}{2}O_2 \tag{10}$$

$\left(\text{Calc. for loss of } \tfrac{1}{2}O_2 \text{ per } PdCl_2 = 9.0\%\right)$

Addition of potassium chloride to the nitrate eutectic caused palladium(II) chloride to dissolve to a red–brown solution at 200 °C, which became deep red at 300°. Nitrogen dioxide was seen to evolve from 350 °C with a palladium(II) chloride : potassium chloride ratio of 1 : 4 (Fig. 3, curve C), but only from 400 °C at a lower rate with a ratio of 1 : 11 (Fig. 3, curve D), which again illustrated the increased stability of chloro-complexes towards the Lux–Flood acid–base reaction [eqn. (8)], though the dark brown insoluble product, after aqueous extraction, was again palladium(II) oxide (found: Pd 85.6%). The weight loss up to 530° of 66.6% was higher than for eqn. (8) because of some melt decomposition

$$NO_3^- \rightarrow NO_2^- + \tfrac{1}{2}O_2 \tag{11}$$

which has been shown to be catalysed by chloride anions [16].

The deep red solution ($PdCl_2$: KCl ratio 1 : 33.5) gave two absorption maxima at 200 °C (28 300 cm^{-1}, ϵ = 270 l mol^{-1} cm^{-1}, and 22 500, 180) which showed a red shift and increased absorbance over those of the yellow solution when no additional chloride was present in the nitrate eutectic (28 300, 150; and 24 000, 155, respectively) suggesting the formation of mixed chloro–nitrate palladium(II) complexes. No other results have been published for palladium(II) solutions in nitrate melts, but palladium(II)

chloride in an all-chloride eutectic (LiCl–KCl at 450°C) had an absorption maximum at 19800 cm^{-1} (ϵ = 278 1 mol$^-$ cm^{-1}) and an absorption edge beyond 27000 cm^{-1} (ϵ = 450 at 27000 cm^{-1}) attributed by the authors [17] to octahedral hexachlorocomplexes with some tetragonal distortion, which may be taken as the limit of the trend with increasing chloride concentration found here. Both the red and the yellow melts, when frozen and then dissolved in water, gave yellow aqueous solutions (maxima at 24500 and 25000 cm^{-1} respectively), which agreed with the trend found for aqueous palladium(II) perchlorate solutions (maximum at 26000 cm^{-1} with no chloride present and at 21000 cm^{-1} with a Pd:Cl ratio of 1:54.3) [18].

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