MATRIX ISOLATION STUDIES ON THE VAPORISATION OF ALKALI-METAL RUTHENATES

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ABSTRACT

The vaporisation of the salts $M_xRuO_4$ ($M=K$, Rb, Cs) has been investigated by classical analytical methods, and by matrix isolation i.r. spectroscopy. For all three systems, the principal ternary vapor species is identified as $MRuO_3$, and a planar ($C_{2v}$) structure is proposed based on a detailed vibrational analysis involving both ruthenium and oxygen isotopic structure. Subsequent analysis of the solid sublimate, however, revealed that a disproportionation of this Ru(V) species occurs to form $RuO_2$ and ruthenate(VI) ($RuO_4^{2-}$).

INTRODUCTION

There is considerable current interest in the chemistry of ruthenium and its compounds, generated in part by the need to understand and predict the speciation of this element if released inadvertently from nuclear reactors. In particular, considerable attention has been focussed on high temperature species, and data are now available for the four binary molecular oxide species $RuO$, $RuO_2$, $RuO_3$, and $RuO_4$ (1-5). However, although alkali metal ruthenates and per-ruthenates are well known in the solid state, there appears to be only one account describing possible ternary species which might be present in the high temperature vapors above these systems. This paper, by Cordfunke et al. (6), is concerned with transpiration studies on cesium ruthenate(VI) in oxygen atmospheres, and concludes, on the basis of analytical data on the sublimate, that the ternary species present in the vapor is molecular Cs$_3$RuO$_4$.

The combination of matrix isolation and i.r. spectroscopy has led to the identification and subsequent characterisation of numerous high temperature chemical species, and using this strategy we have studied the vaporisation of several alkali-metal ruthenate(VII) and ruthenate (VI) salts $M_xRuO_4$, where $M =$ K, Rb, and Cs, and $x = 1$ or 2. Here, we outline the most significant conclusions arising from our experiments on the ruthenate(VI) systems: a more detailed account of this work will be presented elsewhere (7).
EXPERIMENTAL

The samples of alkali-metal ruthenate(VI) used in this work were prepared by heating well-ground mixtures of the alkali metal carbonate and ruthenium dioxide (M : Ru = 2 : 1) in an alumina crucible according to the recipe described by Fischer and Hoppe (8). All the products were dark green in colour, and their identity was confirmed by powder XRD and elemental analysis for M (flame photometry). $^{18}$O enrichment was effected by isotopic exchange with $\text{H}_2\text{O}$. The principal features of our matrix isolation apparatus have been described elsewhere (9). In these present studies, ruthenate samples were vaporised from silica sample holders at temperatures in the range 800 - 1000 °C, and condensed at ca. 12 K with high purity nitrogen or argon (99.999%, BOC). Deposition times were typically ca. 1 hr., and i.r. spectra were recorded using Perkin-Elmer 983Q or Biorad FTS-65A instruments. During deposition, there was a significant build-up of sublimate on the off-axis walls of the sample tube, and this was subsequently recovered and analysed both qualitatively and quantitatively by flame photometry (M), electronic spectroscopy (Ru), and powder XRD.

RESULTS AND DISCUSSION

Figure 1a shows part of a typical argon matrix spectrum obtained from the vaporisation of $\text{Cs}_2\text{RuO}_4$ at ca. 800 °C. The three bands denoted A at 905, 839, and 745 cm$^{-1}$ maintained a constant intensity ratio over a wide range of experiments, and are assigned to a single species. The weaker feature B at 792 cm$^{-1}$ exhibits a variable relative intensity, and its assignment is discussed elsewhere (7). In nitrogen matrices, the bands denoted A appear at 907, 849, and 752 cm$^{-1}$.

Figure 1b shows the corresponding argon matrix spectrum obtained from a sample of 18-oxygen enriched $\text{Cs}_2\text{RuO}_4$. The bands at 905 and 839 cm$^{-1}$ now appear as doublets, with accompanying features at 863 and 822 cm$^{-1}$ respectively, whilst the 752 cm$^{-1}$ feature forms part of a well-defined triplet. 18-oxygen enrichment studies were also carried out on the potassium salt, and Table I summarises all the frequencies obtained.

Figure 2 shows a typical nitrogen matrix spectrum of the bands due to A under higher resolution. The structure present on the highest frequency feature at ca. 907 cm$^{-1}$ is due to the presence of naturally occurring ruthenium isotopes (96, 5.5%; 98, 1.9%; 99, 12.7%; 100, 12.6%; 101, 17.1%; 102, 31.6%; 104, 18.6%), and similar structure is partially resolved on the lowest frequency band at ca. 752 cm$^{-1}$. Similar structure was also observed for the rubidium and potassium salts in nitrogen matrices, and Table II summarises the data obtained. No ruthenium structure could be resolved for the central band at ca. 850 cm$^{-1}$. 257
Spectral Interpretation

The presence of clearly resolved ruthenium isotope structure on the highest frequency band shows that species A is likely to contain one atom of ruthenium. The doublet observed on $^{18}$O enrichment (Figure 1b) indicates that this mode involves the motion of essentially one oxygen atom, and its relatively high frequency identifies it as a terminal mode. In contrast, the band at ca. 745 cm$^{-1}$ clearly involves the motion of two equivalent oxygen atoms, which almost certainly occupy bridging positions in view of the comparatively low frequency.

We therefore propose that species A is CsRuO$_3$, and that it exhibits the structure shown in Figure 3. From the above discussion, both planar (C$_3$) and non-planar (C$_2$) structures would be qualitatively consistent with the observed isotope patterns, but we favor the planar model on the basis of a quantitative study of the isotope shifts. The vibrational analysis we adopt is based on our previous characterisation of the molecular KNO$_3$, NaPO$_3$, and CsAsO$_3$, all of which have been shown (9) to adopt the planar bidentate structure proposed in Figure 3.

Using a "stretch-only" force field, and a bond-dipole model for i.r band intensities (9), this analysis satisfactorily reproduces not only the positions of all the ruthenium and oxygen isotopic species observed, but also the relative intensities of the three basic fundamentals. Figure 1c and Table I compare our observed and calculated spectra in the $^{18}$O enrichment studies, whilst Table II summarises the observed and calculated ruthenium isotopic data.

Analysis of sublimate

The sublimate present on the off-axis walls of the sample holder was analysed by powder XRD, u.v./vis. spectroscopy and flame photometry. XRD showed that both RuO$_3$ and ruthenate(VI) were present, and u.v./vis was consistent with an equal distribution of Ru between these forms. The proportion of alkali-metal present was consistent with an overall stoichiometry MRuO$_3$. These analytical results are therefore consistent with vapor transport via a ternary MRuO$_3$ species, which disproportionates to Ru(IV) and Ru(VI) on condensation.

CONCLUDING REMARKS

These experiments clearly demonstrate that under our vaporisation conditions, the principal ternary species in these M/Ru/O systems is MRuO$_3$. This is in contrast to the results recently reported by Cordfunke et al (6), who deduced that the ternary species present in their transpiration studies is molecular Cs$_3$RuO$_4$. Evidently the higher oxygen partial pressures in these latter studies were sufficient to suppress the change in oxidation state from Ru(VI) to Ru(V), which appears to take place under high vacuum. Further experiments are in progress to identify the low frequency modes for molecular M/Ru/O ternary species in order to estimate thermodynamic properties.
ACKNOWLEDGEMENTS

We gratefully acknowledge the financial support of AEA Technology, Winfrith, U.K., and the EEC for this work, and also wish to thank Dr. B. R. Bowsher and Dr. A. L. Nichols for helpful discussions.

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Table I  Observed and calculated infrared band positions for 18-oxygen enriched MRuO₃ species isolated in argon matrices.

| Assignments | CsRu⁶¹⁸O₃ | KLRu⁶¹⁸O₃ |
|-------------|-----------|-----------|
|              | Observed bands | Calculated bands | Observed bands | Calculated bands |
| A₁ (C₃v) M₄¹⁸ORu¹⁶O₂ | 905.6 | 905.6 | 907.9 | 907.9 |
| A' (C₂v) M₄¹⁸ORu¹⁸O¹⁶O | 863.4 | 863.4 | 865.3 | 866.8 |
| A₁ (C₃v) M₄¹⁸ORu¹⁶O₂ | 839.6 | 839.6 | 839.7 | 839.7 |
| A' (C₂v) M₄¹⁸ORu¹⁸O¹⁶O | 821.8 | 822.3 | 821.7 | 822.7 |
| A₁ (C₃v) M₄¹⁸ORu¹⁶O₂ | 744.9 | 744.9 | 746.6 | 746.6 |
| B₁ (C₃v) M₄¹⁸ORu¹⁸O¹⁶O | 722.8 | 722.8 | 724.7 | 724.8 |
| B₁ (C₃v) M₄¹⁸ORu¹⁸O¹⁶O | 709.2 | 708.9 | 711.5 | 710.2 |

† Force constants and geometries used for calculations:

CsRuO₃: \( f_R = 6.76 \text{ mdyneÅ}^{-1}, f_s = 5.19 \text{ mdyneÅ}^{-1}, f_{Rr} = 0.51 \text{ mdyneÅ}^{-1}, f_m = 0.76 \text{ mdyneÅ}^{-1}; \)
\( \alpha = 98^\circ, \beta = 131^\circ \)

KRuO₃: \( f_R = 6.79 \text{ mdyneÅ}^{-1}, f_s = 5.20 \text{ mdyneÅ}^{-1}, f_{Rr} = 0.50 \text{ mdyneÅ}^{-1}, f_m = 0.70 \text{ mdyneÅ}^{-1}; \)
\( \alpha = 94^\circ, \beta = 133^\circ \)
Table II  
Observed and calculated ruthenium isotope structure for MRuO₃ species isolated in nitrogen matrices.

| Assignments | CsRuO₃ | RbRuO₃ | KRuO₃ |
|-------------|--------|--------|-------|
|             | Obs. bands* | Calc. bands† | Obs. bands* | Calc. bands† | Obs. bands* | Calc. bands† |
| A₁ terminal |         |        |        |        |        |        |
| ¹⁰⁴Ru       | 906.1   | 906.0  | 906.7  | 906.7  | 907.2  | 907.1  |
| ¹⁰²Ru       | 907.4   | 907.3  | 907.9  | 907.9  | 908.4  | 908.4  |
| ¹⁰¹Ru       | 907.9   | 908.0  | -      | 908.5  | -      | 909.1  |
| ¹⁰⁰Ru       | 908.5   | 908.7  | -      | 909.2  | -      | 909.8  |
| ⁹⁹Ru       | 909.3   | 909.4  | 909.7  | 909.8  | -      | 910.6  |
| ⁹⁸Ru       | 910.0   | 910.1  | -      | 910.5  | -      | 910.6  |
| ⁹⁶Ru       | 911.5   | 911.6  | 912.0  | 912.0  | -      | 912.9  |
| A₁ bridge |         |        |        |        |        |        |
| ¹⁰⁴Ru       | -       | 848.2  | -      | 848.3  | -      | 847.2  |
| ¹⁰²Ru       | 848.8   | 848.8  | 849.1  | 849.1  | 847.8  | 847.8  |
| ¹⁰¹Ru       | -       | 849.1  | -      | 849.5  | -      | 848.1  |
| ¹⁰⁰Ru       | -       | 849.5  | -      | 849.9  | -      | 848.4  |
| ⁹⁹Ru       | -       | 849.8  | -      | 850.3  | -      | 848.8  |
| ⁹⁸Ru       | -       | 850.1  | -      | 850.6  | -      | 849.1  |
| ⁹⁶Ru       | -       | 850.7  | -      | 851.4  | -      | 849.7  |
| B₁ bridge |         |        |        |        |        |        |
| ¹⁰⁴Ru       | 750.7   | 750.8  | 752.4  | 752.2  | 751.8  | 751.7  |
| ¹⁰²Ru       | 751.9   | 751.9  | 753.3  | 753.3  | 752.7  | 752.7  |
| ¹⁰¹Ru       | 752.5   | 752.5  | 753.7  | 753.9  | -      | 753.2  |
| ¹⁰⁰Ru       | 753.0   | 753.0  | 754.5  | 754.4  | -      | 753.8  |
| ⁹⁹Ru       | 753.4   | 753.6  | -      | 755.0  | -      | 754.3  |
| ⁹⁸Ru       | 754.4   | 754.2  | 755.4  | 755.6  | -      | 754.9  |
| ⁹⁶Ru       | 755.0   | 755.4  | 756.5  | 756.7  | 755.9  | 756.1  |

* Resolution = 0.6 cm⁻¹, frequency precision = ±0.1 cm⁻¹
† Force constants and geometries used for calculations

CsRuO₃: \( f_s = 6.79 \text{ mdyneÅ}^{-1}, f_1 = 5.30 \text{ mdyneÅ}^{-1}, f_{3s} = 0.51 \text{ mdyneÅ}^{-1}, f_n = 0.78 \text{ mdyneÅ}^{-1}, \alpha = 98°, \beta = 131° \)

RbRuO₃: \( f_s = 6.82 \text{ mdyneÅ}^{-1}, f_1 = 5.31 \text{ mdyneÅ}^{-1}, f_{3s} = 0.55 \text{ mdyneÅ}^{-1}, f_n = 0.74 \text{ mdyneÅ}^{-1}, \alpha = 96°, \beta = 132° \)

KRuO₃: \( f_s = 6.80 \text{ mdyneÅ}^{-1}, f_1 = 5.30 \text{ mdyneÅ}^{-1}, f_{3s} = 0.50 \text{ mdyneÅ}^{-1}, f_n = 0.72 \text{ mdyneÅ}^{-1}, \alpha = 94°, \beta = 133° \)
Figure 1  Argon matrix IR spectrum obtained from Cs$_2$RuO$_3$ vaporisation

(a) Survey spectrum of Ru-O stretching region, showing bands assigned to species A and B.
(b) The same spectral region, with ca. 25% $^{18}$O enrichment.
(c) Calculated spectrum, assuming A to be CsRuO$_3$ ($C_{2v}$).
Figure 2: Nitrogen matrix IR spectra of species above Cs₂RuO₄, showing Ru isotope structure.
Figure 3  Proposed Structure for Molecular CsRuO₂.