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Low-temperature fluorination of ruthenium and osmium di- and tetra-oxides

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Abstract

The fluorination of ruthenium dioxide, RuO_2, and osmium di- and tetra-oxides, OsO_2 and OsO_4, has been studied at ambient temperature using fluorinating agents of variable strength such as chlorine trifluoride ClF_3, bromine pentafluoride BrF_5 or krypton difluoride KrF_2. The results of this study and those previously obtained on the fluorination of ruthenium and osmium tetroxides (RuO_4, OsO_4) are compared and discussed.

The reaction of RuO_2 with KrF_2 in HF solution leads to the ruthenium(V) dioxygenyl salt, $O_2^+RuF_6^-$, and that of OsO_2 to osmium oxide pentafluoride, $OsOF_5$. This oxide fluoride also results from the reaction of OsO_2 or OsO_4 with liquid ClF_3. However, osmium trioxide difluoride, OsO_3F_2, and small quantities of osmium dioxide tetrafluoride, OsO_2F_4, are formed at intermediate stages of the fluorination of OsO_4 by ClF_3. A slow reaction takes place between liquid BrF_5 and OsO_4 to yield OsO_3F_2 as the sole osmium derivative.

A large excess of KrF_2 or its derivative cation KrF^+ in HF solution leaves $OsOF_5$ unreacted.

In contrast to the strength of the metal–oxygen bonds generally observed for the oxide fluorides of osmium in high oxidation states, the weakness of the corresponding Ru–O bonds is the rule. The differences between the fluorination pathways of the oxides of ruthenium and those of osmium are thus explained.

Introduction

When combined with strongly electronegative elements such as oxygen or fluorine, ruthenium and osmium can be oxidized up to oxidation state +8. However, several of the oxide fluorides for which the fluorine and oxygen contents would correspond to the formal oxidation state +6, +7 or +8 for the two metals are still unknown. These deficiencies, which are more numerous for ruthenium, may be due either to the instability of the corresponding oxide fluoride, or to improper reaction conditions. The usual method used to prepare oxide fluorides consists of fluorinating the oxides with fluorine. However, the use of molecular fluorine very often requires high-temperature conditions, and the obvious drawback is that thermally unstable compounds may not be detected.

A more suitable route involves using strong fluorinating agents such as halogen fluorides, krypton difluoride or its derivative cations. Especially when carried out in solution in compatible solvents such as hydrogen fluoride (HF) or halogen fluorides, fluorination can take place at, or below, ambient temperature. Under such reaction conditions even thermally unstable molecules can be prepared.

This paper reports on recent results obtained in that connection for ruthenium dioxide and for the di- and tetra-oxides of osmium. These results are discussed together with those previously obtained on the low-temperature fluorination of ruthenium and osmium tetroxides.

Experimental

General procedure, characterization and materials

Volatile materials were manipulated in a metal vacuum line equipped with Teflon-FEP U-tubes with metal valves. Prior to handling the moisture-sensitive compounds, the system was passivated with chlorine trifluoride. The reactions were carried out in a sapphire or Teflon-FEP tube equipped with metal valves, or in a device made up of a 6-mm o.d. Teflon-FEP U-tube with a side arm, itself made up of a 90° bent 4-mm o.d. Teflon-FEP U-tube fused to the 6-mm o.d. tube and two Monel valves attached to the U-tube. This system allowed the transfer of volatile materials into the reaction tube under dynamic vacuum. Moisture-sensitive non-volatile materials were transferred in the

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dry atmosphere of a glove box. Infrared spectra were recorded in the range 4000–200 cm^{-1} using a Perkin-Elmer model 283 spectrophotometer. A 10-cm path cell made of Monel metal with silver chloride windows and Teflon gaskets was used for the gases. Spectra of solids were obtained using dry powders pressed between AgBr or AgCl windows in an Econo press (Barnes Engineering Co.). Raman spectra were recorded on a Coderg model T800 spectrophotometer using the 647.1 nm exciting line of a Kr ion model 2016 Spectra Physics laser or the 514.5 nm exciting line of an Ar ion model 2016 Spectra Physics laser filtered with a Coderg premonochromator. In order to prevent their decomposition by the laser beam, the solids contained in the side arm of the reaction tube or in 2-mm o.d. glass capillaries were immersed in liquid nitrogen. X-Ray diffraction powder patterns of the samples sealed in 0.5-mm o.d. quartz capillaries were obtained using a Philips camera (diameter 11.46 cm) with Ni-filtered Cu Kα radiation. Elemental analyses were performed by Mikroanalytische Laboratories, Elbach, Germany. The amount of oxygen among the volatiles at −196 °C was determined by exposing them to silicon powder at −196 °C. Under these conditions, only fluorine reacts to yield SiF_4. The $O_2/Kr/SiF_4$ mixture was then trapped at −210 °C with a liquid nitrogen slush, and the oxygen pumped off. The amount of oxygen was deduced from the decrease of pressure measured at ambient temperature in the same volume.

Anhydrous ruthenium dioxide, RuO_2, was obtained by heating the hydrate, $RuO_2 \cdot xH_2O$ ($x \sim 2$) (from Merck), at 700 °C for 3 h. Anhydrous osmium dioxide, OsO_2, was prepared by the reaction of osmium metal (from Compagnie des Métaux Précieux) with oxygen (from l'Air Liquide) at 600–630 °C [1]. Osmium tetroxide, OsO_4 (from Merck), was transferred and stored over P_2O_5. The fluorine (from Union Carbide) used for the preparation of krypton difluoride, KrF_2, was passed over NaF to remove HF, and krypton (from l'Air Liquide) was used without purification. The synthesis of KrF_2 was accomplished as previously described [2]. Commercial HF (from Union Carbide) was dehydrated over bismuth pentafluoride before use [3], while chlorine trifluoride, ClF_3, arsenic pentafluoride, AsF_5, and bromine pentafluoride, BrF_5 (from Comurhex) were purified by trap-to-trap distillation, and BrF_5 was then stored over NaF.

Reaction of RuO_2 with ClF_3

A 0.2076 g (1.560 mmol) amount of RuO_2 was loaded in a dry box into a sapphire tube. In order to avoid loss of the finely divided RuO_2 powder, the tube was evacuated on the vacuum line through a porous Teflon-FEP filter. Hydrogen fluoride (2.123 g) and 0.3794 g (4.104 mmol) of ClF_3 were successively condensed into the tube at −196 °C. The mixture was slowly warmed up to ambient temperature and then stirred for 3 d. The Raman spectrum of the resulting solution showed lines corresponding to ClF_3 [4] and indicated the presence of ClO_2F [5] in trace amounts. After evacuation of the volatiles, the black solid residue, which was analyzed for its Ru and F contents, indicated that no significant fluorination had taken place. Apart from a few weak extra lines, the X-ray diffraction powder pattern of this residue was identical with that for RuO_2 [6]. Neat ClF_3 at reflux at 120 °C for 1 d also left RuO_2 unreacted.

Reaction of RuO_2 with KrF_2 in HF solution

A 0.194 g (1.458 mmol) amount of RuO_2 was loaded in a dry box into a sapphire tube. Hydrogen fluoride (1.44 g) and 1.346 g (11.05 mmol) of KrF_2 were successively condensed into the tube at −196 °C. The mixture was slowly warmed up to ambient temperature and stirred for 3 d. A deep-orange solution with a red–brown solid was obtained. Probably due to a strong absorption in the region of the exciting line (647.1 nm), a satisfactory Raman spectrum could not be obtained for this solution. The volatiles, which were evacuated at −196 °C and analyzed for their oxygen content (see above), did not contain this element. The remaining volatiles were evacuated at −78 °C. The Raman frequencies of the deep-red solid residue recorded at −196 °C corresponded within experimental accuracy to those of the dioxygenyl salt $O_2^+RuF_6^-$ [7]. It was noticed that in the absence of cooling, the samples, which were contained in glass capillaries, decomposed in the laser beam (647.1 nm exciting line). The Raman spectra of the decomposition product recorded at −196 °C with the 514.4 nm exciting line indicated that it was RuF_5 [8]. The samples also decomposed in the beam of the infrared spectrophotometer so that the spectrum recorded contained bands due to RuF_5 [9]. The X-ray diffraction powder pattern of the product corresponded to that of $O_2^+RuF_6^-$ [10]. It is worth pointing out that neither the Raman nor the infrared spectra showed bands that could be assigned to Ru–O vibrations [11]. This rules out the possibility that the product was the hypothetical dioxygenyl salt $O_2^+RuOF_5^-$, the X-ray diffraction powder pattern of which would probably be similar to that of $O_2^+RuF_6^-$.

Reaction of OsO_2 with ClF_3

A 0.159 g (0.717 mmol) amount of OsO_2 was loaded in a dry box into the Teflon-FEP reaction tube. Then 0.524 g (5.671 mmol) of ClF_3 was added by condensation at −196 °C. The solution, whose color progressively turned green–brown, was kept at ambient temperature for 2 d. The Raman spectrum of this solution indicated the presence of $OsOF_5$ [12]. The gaseous fraction above the solution at ambient temperature, which was analyzed by infrared spectroscopy and microsublimation [13], contained O_2, ClO_2F, ClF, ClF_3 and minor quantities of Cl_2, $OsOF_5$ and ClO_3F, but no OsF_6. The volatiles were evacuated under vacuum at −78 °C. However, they could not be completely removed from the Teflon-FEP walls at this temperature, so that the weight of the solid recovered (0.261 g) was more than that expected (0.215 g) from the amount of OsO_2. The Raman spectrum of the emerald-green solid product showed that it only contained $OsOF_5$ [12].

Reaction of OsO_4 with ClF_3

A 1.1335 g (4.459 mmol) amount of OsO_4 was condensed at −196 °C into the Teflon-FEP reaction tube. Then 0.784 g (8.482 mmol) of ClF_3 was added by condensation at the same temperature. The solution, which turned red–orange upon warming to ambient temperature, was left at this temperature for 1 d. The Raman spectrum of the resulting solution showed bands corresponding to ClF_3 [4], $OsOF_5$ [12] and indicated the presence of ClO_2F [5]. Evaporation of the volatiles was carried out in two steps: at −78 °C to eliminate the excess of ClF_3 and the other volatiles at this temperature; and at −10 °C to evaporate $OsOF_5$. The $OsOF_5$ was collected by passing the volatiles through a Teflon-FEP U-trap at −196 °C. The infrared spectrum of the gas obtained from the vaporization of this fraction showed the presence of ClO_2 [14] besides that of $OsOF_5$ [15]. The yellow solid residue obtained after evaporation at −10 °C was identified via its Raman spectrum [16], its X-ray diffraction powder pattern [17] and an elemental analysis as osmium trioxide difluoride, OsO_3F_2. Analysis: Calc. for OsO_3F_2: Os, 68.86; F, 13.76; O, 17.38%. Found: Os, 69.10; F, 13.91; O (by difference), 16.99%. Its weight (1.0185 g) corresponded to 3.688 mmol. The emerald-green solid product corresponding to the volatiles evaporated at −10 °C was further pumped at −78 °C to ensure complete elimination of the ClO_2. It was identified as $OsOF_5$ by Raman spectroscopy [12], and its weight (0.210 g) corresponded to 0.697 mmol. Thus, the conversion yields of OsO_4 into OsO_3F_2 and $OsOF_5$ were 83% and 16%, respectively.

Reaction of OsO_3F_2 with ClF_3

A 0.1694 g (0.613 mmol) amount of OsO_3F_2, prepared from the reaction of ClF_3 with OsO_4, was reacted with 0.6111 g (6.610 mmol) of ClF_3. The reaction was achieved as described above for the ClF_3/OsO_4 system, except that the OsO_3F_2 was loaded into the reaction tube in a dry box. The Raman spectrum of the solution run after a 1-d period at ambient temperature indicated that $OsOF_5$ [12] and ClO_2F [5] had been formed. After 5 d, the gaseous fraction above the solution at ambient temperature, which was analyzed by infrared spectroscopy and microsublimation [13], contained O_2, ClO_2F, Cl_2, ClF, ClF_3 and minor quantities of ClO_3F and $OsOF_5$. Separation of the osmium derivatives was conducted as described above for the ClF_3/OsO_4 system; 0.1296 g (0.430 mmol) of $OsOF_5$ was then isolated. Thus, under these conditions, 70% of the OsO_3F_2 had been converted into $OsOF_5$.

Acidification of ClF_3 by AsF_5 resulted in a much faster reaction: a mixture of $OsO_3F_2/ClF_3/AsF_5$ with the molar ratios 1:8.3:2.7 led to a 100% conversion of OsO_3F_2 to $OsOF_5$ in a few hours.

Reaction of OsO_4 with BrF_5

OsO_4 (0.3046 g, 1.198 mmol) was reacted with 2.329 g (13.318 mmol) of BrF_5 as described above for the reaction of OsO_4 with ClF_3. The slow reaction, which took place at ambient temperature, was complete only after 14 d. At this stage the Raman spectrum of the solution indicated that the OsO_4 had been consumed and that no $OsOF_5$ had been formed. The volatiles and excess BrF_5 were evacuated under vacuum successively at −78 °C, −20 °C and at ambient temperature. The solid residue was identified as OsO_3F_2 by Raman spectroscopy [16]. Its weight (0.340 g) was slightly more than expected for a 100% conversion of the OsO_4 (0.331 g). The excess material was undoubtedly due to BrF_5 or other volatile species trapped in the Teflon-FEP walls.

Mixtures of $OsO_3F_2/BrF_5/HF$ with the molar ratios 1:10:53 or $OsO_3F_2/BrF_5/HF/AsF_5$ with the molar ratios 1:10:53:7 did not result in the formation of $OsOF_5$.

Reaction of $OsOF_5$ with KrF_2 in HF solution

The $OsOF_5$ (*c.* 0.7 mmol) obtained from the reaction of ClF_3 with OsO_4 was condensed into a Teflon-FEP reaction tube. Hydrogen fluoride (0.625 g) and 0.266 g (2.18 mmol) of KrF_2 were successively condensed into the tube at −196 °C. The solution was kept at ambient temperature for 2 d during which time the presence of KrF_2 [18] was periodically checked by Raman spectroscopy. Apart from a slow decrease in the KrF_2 concentration from thermal decomposition, no other activity was observed.

Reaction of $OsOF_5$ with KrF_2 and AsF_5 in HF solution

AsF_5 (0.5393 g, 3.174 mmol) was condensed at −196 °C onto the mixture from the preceding reaction. Bubbling occurred upon warming to ambient temperature, and all of the $OsOF_5$ was solubilized. The solution was frozen again at −196 °C and the volatiles evacuated under vacuum. However, after a few minutes, the instability of the salt $KrF^+AsF_6^-$ at ambient temperature [19] resulted in the reaction tube pressure dramatically increasing as attested by a brief leakage through one of the bellows valves. The Raman spectrum of the solution which was run at this stage only showed bands corresponding to $OsOF_5$ [12] and those of AsF_5 in HF solution [20]. The band due to KrF_2 at 463 cm^{-1} [18] had completely disappeared. The reaction which was duplicated in a system equipped with high-pressure needle valves proceeded similarly.

Results and discussion

Fluorination of RuO_2 by ClF_3 in HF solution does not take place at a significant rate at ambient temperature. The use of the more powerful fluorinating agent KrF_2 leads to the dioxygenyl salt $O_2{}^+RuF_6{}^-$. The reaction mechanism scheme may be assumed to be as follows:

$$RuO_2 + 3KrF_2 \xrightarrow{HF} RuF_6 + O_2 + 3Kr \qquad (1)$$

$$RuF_6 + O_2 \xrightarrow{HF} O_2{}^+RuF_6{}^- \qquad (2)$$

These reactions are based both on the nature of the final solid product and on the absence of oxygen in the volatiles at −196 °C. Reaction (2) is in agreement with a study on the vapor transport of dioxygenyl salts [21], from which its was concluded that the sublimation of the salts $O_2{}^+MF_6{}^-$ (M = Pt, Ru, Rh) involved recombination of O_2 and MF_6 after the salt had dissociated into these molecules at higher temperature. From an estimation of the dissociation pressure of $O_2{}^+RuF_6{}^-$, Mallouk [22] inferred a free enthalpy change ΔG of 10 kcal mol^{-1} at 25 °C for reaction (2) in the reverse direction, and from that he calculated that the electron affinity of RuF_6 was 176 kcal mol^{-1}. However, if the same calculation is performed using the more recent value [23] determined for the electron affinity of RuF_6 (149.2 ± 7 kcal mol^{-1}) together with the relevant data used by Mallouk [22], then the free energy change for reaction (2) is found to be positive by 17 kcal mol^{-1} at 25 °C. Clearly, thermochemical data are of no help here because the free energy change of this reaction is certainly only weakly negative, with the absolute value being smaller than experimental error. Fluorination of RuO_2 by KrF_2 in HF solution turns out to be comparable to that of RuO_2 by atomic fluorine [24], since in both cases the product of the reaction is $O_2{}^+RuF_6{}^-$.

It is worth mentioning that the reaction of KrF_2 with RuO_4 has previously been shown [25] to yield ruthenium oxide tetrafluoride $RuOF_4$. Thus, the same fluorinating agent, KrF_2, is capable or replacing both oxygen atoms of RuO_2 but not all those of RuO_4.

Unlike RuO_2, OsO_2 is fluorinated by ClF_3 at ambient temperature. This dioxide is converted quantitatively into $OsOF_5$. This result is comparable with that of the fluorination of OsO_2 by F_2 at 250 °C in a static system [15].

Osmium tetroxide is fluorinated into a mixture of OsO_3F_2 and $OsOF_5$ by ClF_3 at ambient temperature. It is noteworthy that the formation of $OsOF_5$ corresponds to a reduction of osmium from oxidation state +8 to +7. Complementary experiments have shown that the $OsO_3F_2/OsOF_5$ molar ratio in the solid product depends on the reaction conditions: a long contact time, a ClF_3/OsO_4 molar ratio higher than 2 or dilution of ClF_3 with HF favors the formation of $OsOF_5$. The conversion of OsO_4 into OsO_3F_2 may be considered as the fluorination step that corresponds to the substitution of one atom of oxygen by two atoms of fluorine. The transformation of OsO_3F_2 into $OsOF_5$ is less straightforward. It is amazing that osmium dioxide tetrafluoride OsO_2F_4 [26], which could correspond to the substitution of a second atom of oxygen by fluorine atoms, is not the main product of the fluorination. The latter oxide fluoride is probably formed at an intermediate stage of the fluorination, since two weak Raman bands (also found in fresh solutions of this molecule in ClF_3) were observed at 934 and 920 cm^{-1} for both the OsO_4/ClF_3 and OsO_3F_2/ClF_3 systems. Studies of OsO_2F_4 [27] have shown that this oxide fluoride is slowly converted into $OsOF_5$ in ClF_3 solution at ambient temperature. However, the formation of $OsOF_5$ was much slower in the latter case than observed for the OsO_4/ClF_3 system. The rapid initial formation of $OsOF_5$ is explained by a full fluorination of OsO_4 before the intermediate monomer of OsO_3F_2 takes on the polymeric chain structure [28], and thus becomes practically insoluble in ClF_3. Beyond that stage the fluorination rate is dramatically slowed down, and the rate of the fluorination of OsO_3F_2 into OsO_2F_4 is probably similar to that of the transformation of OsO_2F_4 into $OsOF_5$. This transformation of OsO_2F_4 is a little puzzling, since no such event was found to result from prolonged contact of OsO_2F_4 with HF solutions of KrF_2. The transformation could arise through slow oxidation of an oxygen ligand [15] to yield $OsOF_4$ followed by fluorination of this molecule into $OsOF_5$ but, again, this process should also take place in a solution of KrF_2 in HF.

Liquid BrF_5 slowly converts OsO_4 into OsO_3F_2. Bromine trifluoride, BrF_3, was also reported to yield OsO_3F_2 [29]. The reaction with BrF_5 was much slower than with ClF_3 and there was no evidence of any $OsOF_5$ formation. These differences may be ascribed to the reduced fluorinating power of BrF_5 compared with that of ClF_3. However, bearing in mind that BrF_5 and BrF_3 are Lewis bases which are weaker than ClF_3 [30, 31], and that for the ClF_3/OsO_4 and ClF_3/OsO_3F_2 systems the formation of $OsOF_5$ is enhanced by acidification, it may be inferred that the $ClF_2{}^+$ ion is involved in the transformation of OsO_3F_2 into $OsOF_5$ via OsO_2F_4.

This is consistent with the well-established observation that cations are stronger fluorinating oxidizers than the corresponding parent molecule [32].

Osmium oxide pentafluoride did not react with KrF_2 in HF solution, and neither oxygen elimination to yield OsF_6 (or a hypothetical higher fluoride) nor fluorination into $OsOF_6$* occurred. As far as the combined action of KrF_2 and AsF_5 is concerned, the formation of the powerful fluorinating cation KrF^+ was attested by the decomposition of KrF_2 which followed the addition of AsF_5 to the $KrF_2/OsOF_5/HF$ mixture. $OsOF_5$ was again left unreacted in the latter case.

Conclusions

This work forms part of an ongoing study at Saclay on transition metals in high oxidation states. The preliminary concern was the fluorination of ruthenium oxides. However, it soon became obvious that due to their relative stability the oxide fluorides of osmium were also of interest for comparison. It may be assumed that well-characterized osmium oxide fluorides have their homologues with ruthenium, even if they only exist as transient species for the latter. As an example directly related to the present work on the OsO_4/ClF_3 system, the fluorination of RuO_4 by ClF_3, which had been found to yield $ClO_2{}^+RuF_6{}^-$ [35], might involve the intermediate species $[RuO_3F_2]$ or $[RuOF_5]$. The presence of RuF_5 in the RuO_4/ClF_3 system [35] would then result from the instability of the Ru–O bonds in these hypothetical oxide fluorides. It should also be noted that the action of BrF_5 on RuO_4, unlike that on OsO_4, has not been reported to yield an oxide fluoride, but most likely the Ru^V derivative $BrF_4{}^+RuF_6{}^-$ [29].

Similarly, the fluorination of RuO_4 by KrF_2 in HF solution, which was reported to yield $RuOF_4$ [25], may do so through the intermediate species $[RuO_2F_4]$ followed by breaking of an Ru–O bond. It should be pointed out that the remaining oxygen atom in $RuOF_4$ is certainly not strongly bound to the metal since this compound decomposes into RuF_4 at 65–75 °C [36], and its metal–oxygen stretching vibrational frequency is relatively low (900 cm^{-1}) [25] compared with its homologue in $OsOF_4$ (1009 cm^{-1}) [16].

Finally, the fluorination of OsO_2 by KrF_2 in HF solution does not go beyond the $OsOF_5$ stage whereas, due to the weakness of the Ru–O bond in the hypothetical $[RuOF_5]$, that of RuO_2 goes all the way to the hexafluoride RuF_6, which then reacts with the liberated oxygen.

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*The new crystalline compound resulting from the fluorination of OsO_4 by KrF_2, which on the basis of incomplete characterization was initially described as $OsOF_6$ [33], has now been definitively characterized as *cis*-OsO_2F_4 [26, 28]. Recent calculations for $OsOF_6$ have shown that this molecule is unlikely to exist [34].

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