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Reactions of Ruthenium(III) and -(IV) Chlorocomplexes with Nitrogen Oxides NO and NO_2

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Abstract

Ruthenium chlorocomplexes in the II, III and IV oxidation states are allowed to react with either NO or NO_2. The reactions are followed by spectrophotometry and the products are characterized by IR spectra. In any condition the lower oxidation states oxidize to Ru(IV). The dinuclear complex $[Ru_2OCl_{10}]^{4-}$ reacts only when the conditions permit its depolymerization. In any case the product of the complexation is a complex of $RuNO^{3+}$.

The reaction with NO_2 in 0.5 mol/l HCl gives a complex which is identified as $[RuNOCl_4NO_3]^{2-}$ which is unstable (versus oxidation) in water. The solution containing HCl 3 mol/l represent a redox limit between Ru(III)/Ru(IV) and N(I), N(II), N(III) as Ru(III) is partially oxidized by NO and Ru(IV) is partially reduced by NO. The systematic oxidation of Ru(III) by NO and, as a consequence, the formation of $RuNO^{3+}$ from Ru(IV) and NO lead to some reflexions on the electron repartition in this particular entity.

Introduction

Ruthenium nitrosyl complexes have been widely studied because of their importance in catalytic processes and in nuclear fuel retreatment. The electronic structure, the oxidation state of ruthenium and the nature of the complex species have given rise to a lot of papers, reviewed in ref. 1.

The preparations of the initial $RuNO^{3+}$ moiety are made without any special care about the ruthenium starting materials, RuO_4 [2], K_2RuO_4 [2] as well as hydrated $RuCl_3$ are used [2, 3]. $RuNO^{3+}$ is then separated from the bulk by precipitation of the hydroxide $RuNO(OH)_3$ [4] or some polymeric species. The solid is used to prepare the solutions, generally nitric ones, which are left for a fortnight [5] to ensure equilibrium is reached.

We have been interested in ruthenium chemistry for a long time, especially in the non-complexed ruthenium(IV) solutions [6] and the chlorocomplexes [7, 8].

The use of the chlorocomplexes, $K_2RuCl_5(H_2O)$, K_2RuCl_6 or $K_2Ru_2OCl_{10}$, allows the study of the role of the oxidation number of the ruthenium and the role of the degree of condensation of the ion, in the reaction of formation of the $RuNO^{3+}$ entity.

Identification of the Species

One particular difficulty of the aqueous solution studies is the recognition of the actual species. The method must not alter the nature of the species, chlorocomplex, nitrosyl complex, mono- or polymeric. From this point of view spectroscopic methods are the most convenient.

With UV–Vis spectrometry the separation of the species is poor. All the UV bands are superimposed; in the visible region the bands are broad and lie in a narrow range of wavelengths around 480 nm. The ϵ values vary from 700 to 6000 for the precursors and only 50 for the studied species. So in a mixture, only the precursors can be identified undoubtedly.

Most of the species have been studied in their solid state and the IR spectra are given in the literature [9–13] (Table 1). As we work in aqueous solution we have to eliminate the water to obtain the spectra. We have settled on the following method: a small volume of solution (e.g. 5 ml) is evaporated at about 35 °C or less under reduced pressure. This operation takes about 10 min, then the residue is pelleted in KBr. We have stated that the nitrosyl complexes of ruthenium were, as generally for ruthenium(III) and (IV) complexes, poorly labile and not drastically modified by the treatment.

Experimental

We have used nitrogen monoxide and nitrogen dioxide. The monoxide was provided by l'Air Liquide, it was 99% pure and was bubbled in an alkaline solution before use. The dioxide was from Mathieson, it was 99.5% pure.

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TABLE 1. Main IR frequencies between 200 and 2000 cm^{-1}

Compounds	IR frequencies (cm^{-1})					
		1700	1400	1100	800	500
$K_4Ru_2OCl_{10}$ [9]				887w		327vs 278s
K_2RuCl_6 [10]						345s
$K_2RuCl_5(H_2O)$ [11]		1550w				332s 308s
$K_2RuNOCl_5$ [12]	1910s				604w 586w	338vs 288s
$[RuNOCl_4NO_3]^{2-}$	1900s	1530s	1290s	980s	590w	335s
[this work]			1390s	832s		
Free NO_3^- [13]			1390vs	831s	720s	
O-bound NO_3^- [13]		1531–1481	1290–1253	1034–970	800–781	

The starting salts K_2RuCl_6 and $K_2RuCl_5(H_2O)$ were prepared according to ref. 14, $K_4Ru_2OCl_{10}$ according to ref. 9.

The blue ruthenium(II) chloride solutions were prepared by electrolysis of solutions of chlorocomplexes of Ru(III) or (IV) at a controlled potential of –0.50 V/SCE [15]. The solutions are a mixing of Ru(II) and (III) in the ratio 4/1 respectively and are used without purification.

The ruthenium concentration was varied, for spectrophotometric convenience, from 5×10^{-3} to 10^{-2} mol/l.

The gases were bubbled through the solutions at ambient temperature or at boiling temperature under reflux. The results did not change whether argon or nitrogen was used as the inert gas, but nitrogen was prefered. The durations given in the text are for comparison only, they have no kinetic value.

Results

Reactions with NO

Hydrochloric acid 0.5 mol/l

At boiling temperature. Whatever the oxidation state of ruthenium, the first step leads to the $[Ru(OH)_2Cl_4]^{2-}$ species. For the Ru(II) blue solution heating causes a spontaneous oxidation to Ru(III), then the very first bubble of NO oxidizes it to Ru(IV). The same reaction occurs when Ru(III) is used as the starting material.

The visible spectrum of the solution corresponds to the $[Ru(OH)_2Cl_4]^{2-}$ ion which is the main species of Ru(IV) under these conditions [16].

As the addition of NO is continued the reaction progresses and goes to completion within 30 min for 50 ml of a solution containing 5×10^{-3} mol/l of ruthenium. The disappearance of $[Ru(OH)_2Cl_4]^{2-}$ is easily followed by visible spectrophotometry. The ϵ of $[Ru(OH)_2Cl_4]^{2-}$ and of the nitrosyl complex are so widely different that small traces of the precursor can be detected. The final solution presents the spectrum of the $[RuNOCl_4(H_2O)]^-$ species [17]. After evaporation we obtained the spectrum of the salt $K_2RuNOCl_5$ [12, 18]. The IR nitrate ion bands cannot be pointed out in any of the experiments.

At ambient temperature. Clearly Ru(II) is oxidized to Ru(III) by NO and Ru(III) is oxidized to Ru(IV). Then the chloride of $RuNO^{3+}$ is formed but its formation cannot be achieved as in the previous part. Another difference is that the solutions prepared from $K_4Ru_2OCl_{10}$ do not react at all. The equilibrium between the chlorocomplexes has not been reached; the species in solution is still a dinuclear one.

Hydrochloric acid 3 mol/l

At boiling temperature. The phenomena are similar to these already described (*vide supra*). The formation of the $RuNO^{3+}$ entity is slower and slower.

At ambient temperature. Many important changes arise under these conditions. In the solutions prepared from K_2RuCl_6 (Ru(IV)) we observe a fast and quite complete (90%) reduction of the ruthenium while NO is bubbled. Ru(III) chlorocomplexes can be easily identified from their visible spectrum (Fig. 1). If the flow of NO is stopped, oxidation of Ru(III) begins and can grow up to 25% in 24 h in a stoppered vessel.

In the solutions prepared from $K_2RuCl_5(H_2O)$ bubbling NO causes partial oxidation of Ru(III) into Ru(IV) chlorocomplexes. If the vessel is left stoppered the ratio of oxidized Ru(III) reaches 25% in 24 h.

If NO is flowed continuously both kinds of chlorocomplexes disappear simultaneously. The reaction never goes to completion. The IR spectra of the evaporates of the solutions show $K_2RuNOCl_5$ beside some chlorocomplexes of Ru(III) and Ru(IV) and sometimes weak NO_3^- bands.

No reaction is observed for the solutions of $K_4Ru_2OCl_{10}$.

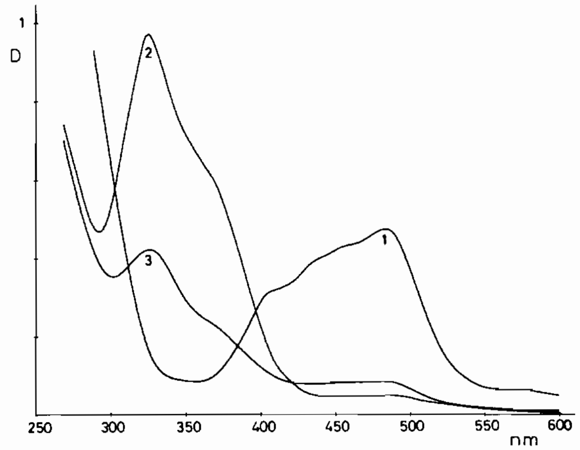

Fig. 1. Visible spectra of ruthenium solutions; HCl 3 mol/l; cells 0.1 cm. Curve 1, Ru 10^{-3} mol/l K_2RuCl_6; 2, Ru 5 X 10^{-3} mol/l $K_2RuCl_5(H_2O)$; 3, Ru 5 X 10^{-3} mol/l at the end of the reaction with NO.

Reactions with NO_2

We worked only with 0.5 mol/l solutions of hydrochloric acid .

At boiling temperature the results are the same as with NO. The time of reaction is half as long. Owing to the dismutation of NO_2 the solutions contain important concentration of NO_3^- ions. The determination of NO_3^- by the Kjeldhal method gives a concentration of 1 mol/l (Ru 5 X 10^{-3} mol/l) when the reaction is achieved. The free NO_3^- ions are also well characterized by the IR spectrum. At ambient temperature the reaction seems to develop similarly, after about 20 min the precursors have disappeared. Nevertheless the IR spectrum of the evaporate (Table 1) shows new bands. These bands are due to bound nitrate ions. If dissolved again the obtained solid gives unstable solutions producing Ru(IV) chlorocomplexes.

The results are summarized in Table 2.

Discussion

The last result is of interest. The visible spectrum indicates unambiguously that neither Ru(IV) nor Ru(III) chlorocomplexes are still present. The IR spectrum looks like a mixture of the $[RuNOCl_5]^{2-}$ ion and bound NO_3^- ions. The 335 cm^{-1} frequency corresponds to the in plane symmetric vibration of $RuCl_4$ in the Ru(IV) chlorocomplex as well as in the nitrosyl one.

If $K_2RuNOCl_5$ is dissolved in nitric hydrochloric solutions and then evaporated, the residue gives the same spectrum. We have assumed this complex to be *trans*-$[RuNOCl_4NO_3]^{2-}$.

In the case of the nitrosyl nitrato complexes of ruthenium, Scargill *et al.* [5] have stated that this *trans* position could not be occupied by a nitrate ion, the four equatorial ones making it too labile. Here the four equatorial chloride ions allow this position to be occupied only at low temperatures whereas heated, under NO_2 flow, the complex disappears giving $[RuNOCl_5]^{2-}$. Put in solution in water this complex decomposes into Ru(IV) chlorocomplexes and nitrogen oxides. Most probably the NO–Ru–NO_3 chain is responsible for this instability.

Before discussing the results obtained with NO we look at the ruthenium chlorocomplexes equilibria. The kinetics of aquation are relatively slow and the

TABLE 2. The reactions between ruthenium compounds and nitrogen oxides (slow/fast refers to the formation of $RuNO^{3+}$)

Precursors	Nitrogen oxide	Conditions of reaction			
		HCl 0.5 mol/l		HCl 3 mol/l[a]	
		ambient temperature	boiling temperature	ambient temperature	boiling temperature
$K_4Ru_2OCl_{10}$ (Ru(IV))	NO	no reaction	fast	no reaction	slow
	NO_2	reaction	fast		
K_2RuCl_6 (Ru(IV))	NO	slow	fast	reduction and slow	reduction and slow
	NO_2	fast $[RuNOCl_4NO_3]^{2-}$	fast		
$K_2RuCl_5(H_2O)$ (Ru(III))	NO	oxidation and slow	oxidation and fast	oxidation and slow	oxidation and slow
	NO_2	oxidation and fast	oxidation and fast		

[a] No reaction goes to completion.

species in solution are not the same at ambient as at boiling temperature. For a 5×10^{-3} mol/l solution of Ru in a 3 mol/l hydrochloric acid solution the equilibrium must be

$$H_2O + [Ru_2OCl_8(H_2O)_2]^{2-} \rightleftharpoons 2[Ru(OH)_2Cl_4]^{2-} + 2H^+$$

rather displaced towards the left [16]. Thus at boiling temperature the equilibrium state is reached or nearly, whereas it is not at ambient temperature. The solution made from $K_4Ru_2OCl_{10}$ is rich in dinuclear species such as $[Ru_2OCl_{10}]^{4-}$ to $[Ru_2OCl_8(H_2O)_2]^{2-}$. In solution prepared with K_2RuCl_6 the right term prevails. Likewise the solution prepared with the Ru(III) salt $K_2RuCl_5(H_2O)$ contains only mononuclear species, mainly $[RuCl_5(H_2O)]^{2-}$.

We can now examine the results (Table 2) of the formation of $RuNO^{3+}$ in the different conditions. The dinuclear species does not react with NO in 0.5 mol/l hydrochloric acid and, *a fortiori*, in 3 mol/l solutions. The fact that we obtain a relatively fast reaction between $K_4Ru_2OCl_{10}$ and NO_2 at ambient temperature is probably due to the important concentration of nitrate ions produced by NO_2. The dechloration is reinforced by the nitrate complexation and the mononuclear form is favoured.

At this stage we assume that the reaction between nitrogen oxides and ruthenium chlorocomplexes needs a mononuclear species in solution.

Now if we consider $[RuCl_6]^{2-}$ we observe the same behaviour at ambient temperature; the reaction is faster with NO_2 than with NO. In this complex the reaction of aquation is faster than in $[Ru_2OCl_{10}]^{4-}$ and it reacts slowly with NO. With NO_2 the complexation by the nitrate favours the formation of the $RuNO^{3+}$ entity and we have found the species *trans*-$[RuNOCl_4NO_3]^{2-}$ in the solutions at ambient temperature.

At boiling temperature the chlorocomplex in solution is *trans*-$[Ru(OH)_2Cl_4]^{2-}$ and the reaction is fast with all the precursors.

During the reaction with Ru(III) an oxidation reaction takes place. This phenomenon is more complex in the 3 mol/l HCl solutions. At ambient temperature we observe that Ru(III) is oxidized by NO up to 25% (or more) before/while the $RuNO^{3+}$ is formed. On the contrary the same NO reduces Ru(IV) to a major extent. As the first reaction has been observed in 0.5 mol/l HCl, the second is quite surprising.

Let us consider the redox potentials. For the nitro gen oxides the couples containing NO are

$$2NO + 2H^+ + 2e^- \rightleftharpoons N_2O + H_2O \quad E^\circ = 1.59\ V\ [19]$$

$$2NO + 2H^+ + 2e^- \rightleftharpoons H_2N_2O_2 \quad E^\circ = 0.71\ V\ [20]$$

$$HNO_2 + H^+ + e^- \rightleftharpoons NO + H_2O \quad E^\circ = 0.99\ V\ [19]$$

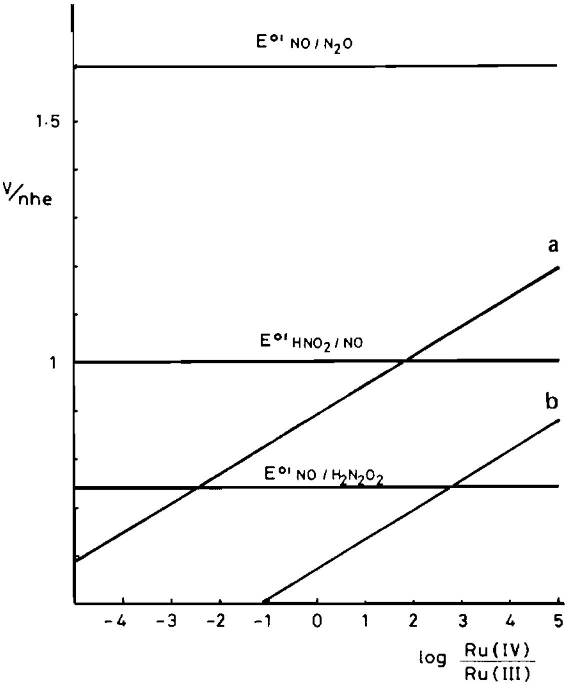

Fig. 2. Comparison of the normal apparent (H^+ 3 mol/l) potential of redox couples of NO involving one electron per NO molecule vs. the redox potential of Ru(IV)/Ru(III) in HCl 2 mol/l (a) and in non-complexing medium (b).

We have retained these couples because they involve only one electron per NO molecule. The potential of the couple Ru(IV)/Ru(III) in hydrochloric acid medium changes with authors and conditions; we have used the value $E^\circ = 0.89$ V in HCl = 2 mol/l [19], in conditions which are not very different to the present ones. We have reported (Fig. 2) a graph of these potentials assuming that the ratio Ru(IV)/Ru(III) varies from 10^{-5}, pure Ru(III), to 10^5, pure Ru(IV).

A first conclusion is the impossibility for the reaction to produce N_2O because we should only observe oxidation of Ru(III), in any case Ru(IV) could be reduced. The two other couples are consistent with the observed phenomena. If the reaction starts from Ru(III) the couple $NO/H_2N_2O_2$ is the most oxidant and produces Ru(IV), on the other hand if the reaction is based on Ru(IV) the reduction is performed by the couple HNO_2/NO. In both cases the products $H_2N_2O_2$ or HNO_2 are not stable and in low concentration; they are not present on the IR spectra. So, whatever the starting ruthenium complexes, the redox reaction arises and reaches an 'equilibrium state' between all the species. The potential of the solution is then about 0.8–0.9 V. The solution is slightly more concentrated in Ru(III) than in Ru(IV), in agreement with the spectrum (Fig. 1).

This study shows that the usual notation Ru(II) NO^+ must be used with care. It is a facility for electron bookkeeping and, in any case, an exhibition of the chemical properties of the ruthenium. The reactions encountered here process always between Ru(III) and Ru(IV).

The redox reactions which obey the thermodynamical data, are fast. They are partial in concentrated HCl solutions and total in diluted ones because of the lowering of the redox potential (in non-complexing medium the potential for the couple $[Ru_4(OH)_{12}]^{4+}/[Ru_4(OH)_4]^{8+}$ is 0.561 V in 1 mol/l $HClO_4$ [21]). As these reactions are fast, we assume they process by outersphere mechanisms or induced electron transfers. This assumption is supported also by the low lability of the ruthenium complexes and the possibility for the ligands Cl^- or OH^- to form bridges for the charge transfer [22].

The second kind of reactions are the reactions of complexation. The formation of a Ru–NO bond needs that one of the previous ligands exchanges against NO, assuming that a square of chloride ions remains bound. In this step the lability of the ligand plays an important role and the replacement is accelerated by saturating the solution with NO. This causes first, the oxidation of Ru(III), so in 0.5 mol/l HCl solutions only Ru(IV) exists and then NO must enter into the coordination sphere of a Ru(IV) atom. In such a case $Ru{-}NO^{4+}$ could be created by the replacement of a π electron donor (Cl^-, OH^-) by a π electron acceptor. This difference in electrophilic character would disturb the previous energy levels and create a new distribution. Whatsoever the orbitals, this complex must reduce to form $RuNO^{3+}$. A reasonable explanation could be the reduction by one NO molecule which is the unique reducer in the solution. The reduction has to be fast to explain the absence, at least on the visible and IR spectra, of $RuNO^{4+}$. So an induced charge transfer between the two NO could be invoked which brings the π^* electron of the reducing NO into the system of the complex. Such reactions between orbitals of the same symmetry are known to be very fast [22] and generate little disturbance; the orbital system of $RuNO^{3+}$ would be then a remembrance of the $RuNO^{4+}$ one. It becomes impossible to dissociate $RuNO^{3+}$ into isolated constituents. However this formula looks too much like the sum Ru^{3+} plus NO that we have a last suggestion to offer. We have seen that Ru(III) is oxidized fast by NO by some remote reaction. In the case of the entity $RuNO^{3+}$ we wonder if this species is an activated complex of an innersphere oxidation mechanism of Ru(III) by NO in which the Franck–Condon restriction could not be met. It seems that the examination of the metal nitrosyl from this point of view could be of interest.

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