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Kinetic and Mechanistic Studies on the Ruthenium Induced Activation of Methylamine to Oxidation

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When aqueous solutions containing $[Ru(NH_2CH_3)_6]^{2+}$ are exposed to oxygen $[Ru(NH_2CH_3)_5(OH)]^{2+}$ is produced as an identifiable intermediate as a result of the slow replacement of co-ordinated methylamine by water, and the subsequent rapid oxidation of this ruthenium(II) aquo complex. The $[Ru(NH_2CH_3)_5(OH)]^{2+}$ ion then undergoes another slow reaction, probably the replacement of another methylamine ligand by water. All subsequent reactions leading to $Ru(CN)_3 \cdot 3H_2O$ are rapid. Rate data are reported, and a mechanism involving β-elimination from co-ordinated methylamine is postulated.

Introduction

In earlier publications[1,2] we have reported the fact that when primary amines are coordinated to ruthenium(II) they are very susceptible to oxidation by molecular oxygen. This process results in the conversion of methylamine to coordinated cyanide, and of higher amines, RCH_2NH_2, to coordinated nitriles RCN. Other authors have reported related observations for ethylenediamine coordinated to ruthenium[3] and iron[4], and for branched amines coordinated to molybdenum[5]. In this paper we report the results of experiments aimed at elucidating the mechanism of the reaction between $[Ru(NH_2CH_3)_6]^{2+}$ and O_2 in water. Several different problems arise when systematic studies are attempted, and so we have been unable to identify all the details of the process.

Experimental

Reagents

The preparation of hexakisamine complexes has previously been reported by us[2]. Solutions containing the chloropentakismethylamineruthenium(III) or bromopentakismethylamineruthenium(III) cations were obtained by dissolving the hexakismethylamineruthenium(II) dibromide in the appropriate concentrated acid and allowing the solutions to oxidise in air[6]. All other reagents used were of Analytical grade. Freshly distilled water was used in all experiments.

Kinetic Studies

Kinetic studies were carried out using two sets of equipment previously described elsewhere[7,8]. The only modification being that reactions were started by allowing a small glass cup, containing solid $[Ru(NH_2CH_3)_6]Br_2$, to drop into a thermostated aqueous solution of the inert electrolyte, K_2SO_4, which had been allowed to stand under an atmosphere of pure oxygen. The reaction solution was then vigorously agitated by stirring or shaking mechanically. In the case of the spectrophotometric studies samples were withdrawn at frequent intervals from a tap at the bottom of the thermostatted reaction vessel, while a reservoir was adjusted to maintain a constant oxygen pressure. Optical density measurements were then made using a Pye Unicam SP500 spectrophotometer. When oxygen consumption was followed, a similar system was employed, with the exception that samples of the reaction solution were not withdrawn.

Other Studies

Ultra violet and visible spectra were obtained using a Pye Unicam SP800 spectrophotometer, with a repeat time of approximately 2½ minutes. Oxygen free aqueous solutions were prepared in a vacuum line system, and transferred from one container to another by using syringes and rubber suba seals.

Results and Discussion

Qualitative Studies

An aqueous solution of $[Ru(NH_2CH_3)_6]Br_2$ reacts with oxygen according to the equation[2]

$$4[Ru(NH_2CH_3)_6]^{2+} + 13O_2 + 4H^+ = 4Ru(CN)_3 \cdot 3H_2O + 12CH_3NH_3^+ + 14H_2O$$

At room temperature, under an atmosphere of pure oxygen, the final ruthenium product begins to precipitate from solution within ten minutes. The reaction proceeds to completion more slowly under air. Information concerning the nature of the intermediates in this reaction can be obtained by repeatedly recording the ultra violet and visible spectra of reacting solutions.

An aqueous solution of the initial complex, prepared and handled under argon shows a weak absorption at 275 nm and another at 375 nm (line 1 of Fig. 1). The spectrum changes slightly with time. The 275 nm peak behaves as an isosbestic point, while the absorption at 375 nm increases slightly. No strong or new bands appear until oxygen is introduced, when a strong band centred on 318 nm rapidly appears. This same band appears quickly if oxygen is admitted to a freshly prepared solution.

A more informative set of spectra occur when a small quantity of air is allowed into the top of a stoppered optical cell, containing an aqueous solution of $[Ru(NH_2CH_3)_6]Br_2$ at room temperature. Some of the repeat spectra from such an experiment are illustrated in Figure 1. Under these conditions the concentration of dissolved oxygen is low, and the reactions occur more slowly than under pure oxygen. For approximately fifteen minutes isosbestic behaviour occurs at 275 nm, while the optical density gradually increases at higher wavelengths. After this period of time, the isobestic behaviour at 275 nm ceases, and a new isosbestic point is observed at 366 nm. At the same time, the strong broad band at 318 nm begins to develop. These results are reproducible, while complexes of other amines behave similarly. Thus, the hexakis-n-butylamineruthenium(II) complex, in water under air, shows an early isosbestic point at 270 nm, and the strong band appears at 320 nm.

These observations show a sequence of reactions is occuring:

$$[Ru(NH_2CH_3)_6]^{2+} \rightarrow B \rightarrow C$$

The starting complex has weak absorption bands at 275 nm and 375 nm, which are seen as shoulders. The complex B also shows weak absorption at 275 nm and has a slightly greater extiction coefficient at 375 nm while C has a much stronger band at 318 nm. Also, oxygen is involved in one or other of the reactions leading to C; probably in the second step.

Taube and his co-workers[9] have shown that $[Ru(NH_3)_5Py]^{2+}$ produces an intense change transfer band at 408 nm. This band can be used[10] to determine the concentration of Ru^{II} amine complexes in the presence of the Ru^{III} analogues at pH values below 9.5. We find that the addition of pyridine to oxygen free solutions of $[Ru(NH_2CH_3)_6]^{2+}$ produces an intense band at 380 nm, which obeys Beer's law. The addition of a slight excess of pyridine to an aqueous solution containing $[Ru(NH_2CH_3)_5Cl]^{2+}$ results in very weak absorption at 380 nm only after considerable time has elapsed. We therefore believe that pyridine may be used in the determination of Ru^{II}

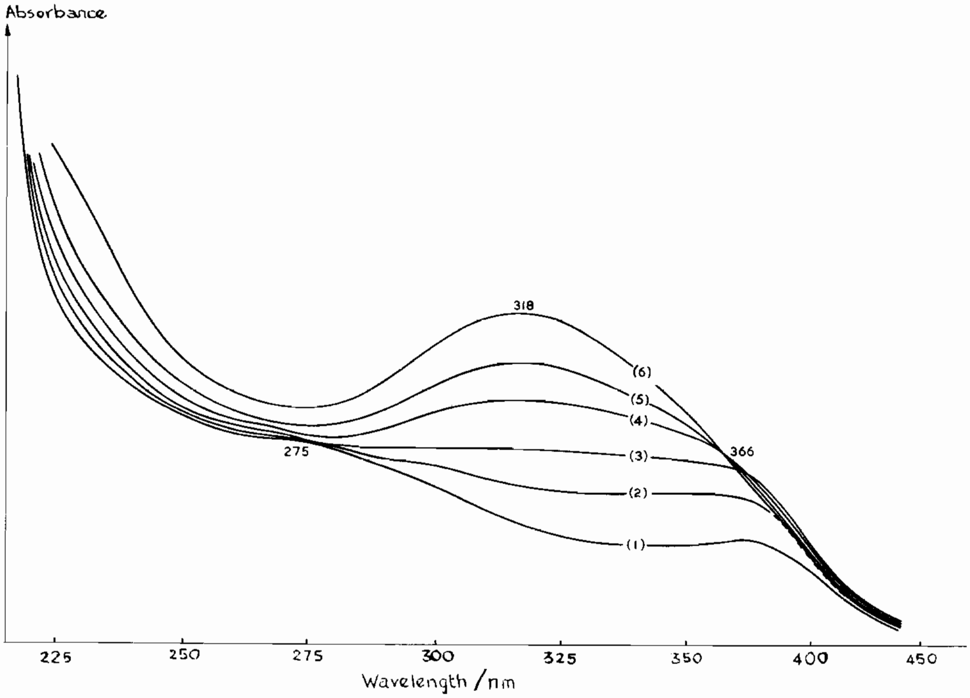


Figure 1. Repeated spectral scans for $[Ru(NH_2CH_3)_6]Br_2$ in water, exposed to a small amount of air. Line 1 corresponds to the solute before exposure to air, lines 2 to 6 were recorded after 5,10, 20,20 and 50 minutes respectively.

concentrations in the amine system. When a series of solutions of $[Ru(NH_2CH_3)_6]Br_2$ are exposed to air and subsequently treated with pyridine after five or more minutes, the optical density at 380 nm corresponds to approximately 40% of the total ruthenium still being in the oxidation state II. This value does not change between periods of five and fifteen minutes.

When solid $[Ru(NH_2CH_3)_6]Br_2$ is added to neutral distilled water to produce a ruthenium concentration of $1 \times 10^{-3} M$, typical of the concentrations used in our experiments, the pH of the solution rises rapidly. Within the time required for complete dissolution of the solid, the pH has reached a steady value of 9.3. This rise is attributed to free methylamine, derived either from ligand dissociation or from slight contamination of the solid sample (see below). At such a pH, disproportionation of ruthenium(III) complexes may be rapid[10], thus preventing a true determination of the ruthenium (II) concentration. Nonetheless, the intermediate labelled C clearly contains ruthenium in a higher oxidation state, probably III.

Although the final product of the oxidation of $[Ru(NH_2CH_3)_6]^{2+}$ contains coordinated cyanide, while complexes containing higher amines yield nitriles, neither B nor C contain cyanide. This may be deduced from the following observations.

Aqueous solutions of $[Ru(NH_2CH_3)_6]Br_2$ and KCN in the ratios 2:1, 1:1, 1:2 and 1:3 do not produce spectra resembling those of B or C, whether under argon or oxygen. The addition of a solution of KCN to a partially reacted solution of the ruthenium complex suppresses, rather than enhances, the absorption at 318 nm. Further, the spectra appearing in the early stages of oxidation of aqueous solutions of hexakis-n-butylamineruthenium(II) bear no resemblance to those described[11] for organonitrilepentakisammineruthenium (III) complexes.

The ligands present in B and C are therefore drawn from methylamine, water, hydroxide and bromide. From an examination of the spectral data summarised in Table I, the formula $[Ru(NH_2CH_3)_5(OH)]^{2+}$ may be confidently assigned to C. An additional point in favour of this assignment is that our kinetic studies provide an estimate of the extinction coefficient at 318 nm. This value, 1600 litre mol^{-1} cm^{-1} compares favourably with the estimate[14] of approximately 1500 litre mol^{-1} cm^{-1} for $[Ru(NH_3)_5(OH)]^{2+}$. Complex B is likely to be $[Ru(NH_2CH_3)_6]^{3+}$, $[Ru(NH_2CH_3)_5(OH_2)]^{2+}$ or $[Ru(NH_2CH_3)_5(OH)]^{+}$. The assignment of one of these formulae is much less reliable than is the case for C. We feel that the available evidence is best fitted by a ruthenium(II) complex, and so we represent B as $[Ru(NH_2CH_3)_5(OH_2)]^{2+}$.

Quantitative Studies

The data described above show that the early stages of the oxidation of $[Ru(NH_2CH_3)_6]^{2+}$ can be studied spectrophotometrically by following the appearances of the 318 nm band of $[Ru(NH_2CH_3)_5(OH)]^{2+}$, while the total reaction could be studied by determining the rate of oxygen consumption. We have carried out both these sets of experiments.

Since $[Ru(NH_2CH_3)_5(OH)]^{2+}$ is an intermediate, whose subsequent reaction leads to the insoluble $Ru(CN)_3 \cdot 3H_2O$, it is not possible to prove directly that the absorption at 318 nm obeys Beer's law. However, this can be shown indirectly. When a series of solutions containing different initial concentrations of $[Ru(NH_2CH_3)_6]Br_2$ are allowed to react with oxygen under identical conditions, we find that the change in optical density over a given time of reaction varies linearly with the initial reagent concentration. Such a dependance will occur if, and only if, Beer's law is obeyed and the reactions leading to $[Ru(NH_2CH_3)_5(OH)]^{2+}$ are first order in ruthenium. The observed dependance of optical density with time does in fact follow first order kinetics.

After a period of reaction varying from seven to ten minutes, $Ru(CN)_3 \cdot 3H_2O$ begins to precipitate from reaction solutions. This effect renders the use of a flow system impractical, and so spectrophotometric readings were made by extracting samples from a separate reaction vessel. The reaction is initiated by adding solid $[Ru(NH_2CH_3)_6]Br_2$ to an aqueous solution of the inert

TABLE I. The Positions of Spectral Maxima for Complexes of Type $[RuL_5X]$ (λ/nm)[a].

Ruthenium Oxidation State	X	L = CH_3NH_2	L = NH_3	Ref. for L = NH_3
III	Cl^-	275, 345	260, 328	6
III	Br^-	410	330, 398	6
III	L		275, 320	12
III	H_2O		275, 375	13
III	HO^-	C has 318	295	14
II	L	275, 375	275(sh), 380–420	13
II	H_2O	B has 275	272	15
II	P_y	380	408	9

[a] Sh represents shoulder.

electrolyte under an oxygen atmosphere. The total ruthenium concentration being in the region of 8 × 10^{-4}M. We were therefore unable to make observations during the first minute of reaction because of the need to ensure rapid and complete dissolution of the solid. Optical density readings were obtained from this time up to the onset of precipitation. Over this period the data fit a first order equation. An iterative least squares programme evaluating both the rate constant and the final optical density was applied to the data. The computed values for the final optical density, expected in the absence of precipitation or slow subsequent reactions, provide the estimate for the extinction coefficient at 318 nm. We may also deduce, since the optical density, before precipitation commences, reaches a value greater than half the expected final value, that the rate constant governing the disappearance of $[Ru(NH_2CH_3)_5(OH)]^{2+}$ must be less than that governing its appearance.

In Table II, the determined rate constants, designated k_1, for runs at different temperatures are recorded. The value of k_1 is constant, within experimental error, over a range of ionic strengths from 5 = $10^{-3}M$ to 0.2*M* at 30° C. We have been unable to determine the dependance of k_1 on either pH or on the concentration of free methylamine, since varying either function produces a marked change in the spectra of the reaction solutions. We also note that, although values of k_1 are reproducible for runs carried out on a single batch of $[Ru(NH_2CH_3)_6]Br_2$, rate constants can differ by up to 30% when samples of reagent from different batches are used. This phenomenon occurs even though the different samples appear to be pure. The studies of oxygen consumption described below also show this feature. Our interpretation of the spectrophotometric observations is presented below, after the data from oxygen uptake experiments have been described.

If a reaction solution remains saturated with oxygen, the rate of reaction can be followed by monitoring the volume change, at constant pressure, of the gas above the solution. We have studied the oxidation of $[Ru(NH_2CH_3)_6]Br_2$ in this way. In our experiments the reaction solution, containing 2 × $10^{-3}M$ ruthenium, is agitated by shaking under oxygen gas, while the volume change in the gas is determined manometrically. By carrying out duplicate experiments at different agitation rates, it is possible to find conditions under which the rate of consumption is independant of the rate of agitation, up to 40° C. Therefore experiments may be undertaken in which the rate of solution of oxygen gas does not play any significant role. Unfortunately, the use of vigorous agitation transmits some mechanical vibration to the manometer of our apparatus This increases the errors in individual readings, and renders the measurement of small volume changes inaccurate. That is, points at the beginning of an oxygen uptake experiment may not be very reliable.

TABLE II. Rate constants derived spectrophotometrically (k_1) and by measuring the rate of uptake of oxygen (k_2), at an ionic strength of 0.1*M*, maintained using K_2So_4. Values quoted are the arithmetic means of duplicate experiments, whose individual values agreed to within 5 per cent.

Temperature/° C	k_1/sec^{-1}	k_2/sec^{-1}
20	–	2.36 × 10^{-4}
25	1.36 × 10^{-3}	2.83 × 10^{-4}
30	1.56 × 10^{-3}	3.69 × 10
35	1.96 × 10^{-3}	4.20 × 10^{-4}
40	2.48 × 10^{-3}	5.42 × 10^{-4}
45	3.09 × 10^{-3}	–
49	3.78 × 10^{-3}	–

A typical plot of oxygen consumption versus time is shown in Figure 2. This plot is characteristic of the curve expected for a series of consecutive steps, where most of the oxygen is used up in the later stages of the sequence. Although it is possible to fit the experimental data to a scheme involving two consecutive pseudo-first order reactions, with most of the oxygen consumed in the second step, the inaccuracy of the early points makes such data fits suspect. In consequence, we have chosen to treat the majority of the curve, but excluding the early points, as a first order reaction. Such a treatment is acceptable when once $\exp(-k_1t)$ becomes essentially zero. In Table II we quote the rate constants (k_2) determined in this way. These values are reproducible in duplicate experiments using the same batch of solid $[Ru(NH_2CH_3)_6]Br_2$, although variations are found between batches prepared at different times. We also find that k_2 is constant, within experimental error, at 35° C over a range of ionic strengths, 5 × $10^{-3}M$ to 0.2*M*.

It is relevant to note that we find no evidence of an initial rapid consumption of oxygen, followed by a slower continuing reaction. It is known[16] that H_2O_2 oxidizes $[Ru(NH_3)_6]^{2+}$ much more slowly than does O_2. If the reaction studied spectrophotometrically is preceded by a rapid oxidation step, an early rapid consumption of one half a mol of oxygen per mol of ruthenium should occur. That is 2/13 of the total oxygen consumption would occur in the early stages of a kinetic experiment. An initial change of this magnitude should be readily detectable. We therefore rule out a rapid oxidation step as the first reaction of $[Ru(NH_2CH_3)_6]^{2+}$.

When free methylamine is added to a reaction solution, in an attempt to study the effect of methylamine on k_2, the behaviour of the reacting system changes. Oxygen consumption does not stop when a ratio of 4 : 13 for Ru : O_2 is reached, but consumption continues slowly until all the excess methylamine has been oxidized. It seems that this oxidation continues to be catalysed by ruthenium in aqueous solution until the precipitation of the very insoluble cyanide removes the metal ions.

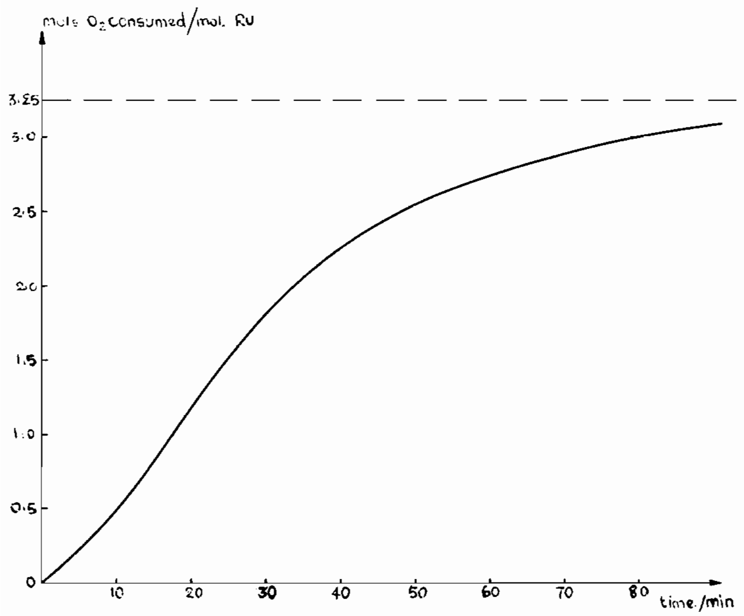


Figure 2. A typical plot of the oxygen consumption of aqueous solutions of $[Ru(NH_2CH_3)_6]Br_2$ exposed to oxygen gas at 1 atmosphere pressure.

Finally, we note that k_2 does not alter when the reaction vessel is shielded from light, even though the reaction between solid $[Ru(NH_2CH_3)_6]Br_2$ and oxygen occurs at a greater rate when exposed to light.

Interpretation of Results

The conversion of $[Ru(NH_2CH_3)_6]^{2+}$ to $[Ru(NH_2CH_3)_5(OH)]^{2+}$ occurs in two stages. Under an atmosphere of pure oxygen one of these steps is much faster than the other, while spectra recorded at low oxygen concentrations show the build up of an intermediate complex. The evidence we have been able to collect suggests that these first two steps are

$$[Ru(NH_2CH_3)_6]^{2+} + H_2O \xrightarrow{k_1} [Ru(NH_2CH_3)_5(OH_2)]^{2+} + CH_3NH_2 \quad \text{(i)}$$

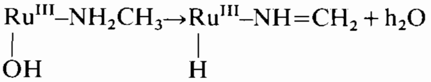
$$2[Ru(NH_2CH_3)_5(OH_2)]^{2+} + O_2 \xrightarrow{\text{fast}} 2[Ru(NH_2CH_3)_5(OH)]^{2+} + H_2O_2 \quad \text{(ii)}$$

k_1 has a value of 1.36×10^{-3} sec^{-1} at 25° C and an activation energy of (9.1 ± 0.5) kcal mol^{-1}. These data refer to a reaction carried out at a pH of approximately 9.3. Most of the studies of related reactions which have been reported have been carried out at pH values below 7, and may not be comparable. For example, the substitution of NH_3 by H_2O in $[Ru(NH_3)_6]^{2+}$ shows a first order dependance on $[H^+]$ in acidic media[17], while the oxidation of $[Ru(NH_3)_6]^{2+}$ and $[Ru(en)_3]^{2+}$ by molecular oxygen has been studied[16] at pH $\leqslant 6.05$. The kinetic parameters reported in these studies are markedly different from those of the reaction studied by us. Due to the different conditions of acidity this is not surprising. The pKa for $[Ru(NH_3)_6]^{3+}$ has been estimated[18] to be 12.4, while the reaction between this complex and nitric oxide in alkaline conditions is postulated[19] to proceed via the conjugate base. A conjugate base mechanism has also been postulated[20] for the base hydrolyses of such complexes. If the presence of base can affect the rates of the reactions of the methylamine complexes, then such an effect may account for our inability to obtain data at other pH values, while the presence of traces of non-coordinated methylamine would explain the differing rate constants for different sample batches.

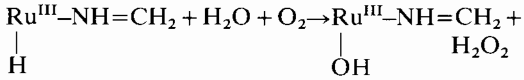
Equation (ii) is immediately followed by another slow step, presumably that described by k_2. This step has an activation energy of (7.7 ± 0.7) kcal mol^{-1}, and $k_2 = 2.83 \times 10^{-4}$ sec^{-1} at 25° C. Since this rate constant is also independant of ionic strength, we may reasonably deduce that it represents either the substitution of a second coordinated methylamine molecule by water, or else the oxidation of a methylamine ligand either by oxygen or in an intramolecular process. This slow step is then followed by several more rapid steps involving the conversion of methylamine to cyanide. Our unsupported guess is that the second slow step in the sequence is

$$[Ru(NH_2CH_3)_5(OH)]^{2+} + H_2O \xrightarrow{k_2} [Ru(NH_2CH_3)_4(OH)(OH_2)]^{2+} + CH_3NH_2 \quad \text{(iii)}$$

We choose this as the reaction described by k_2, since the subsequent oxidation steps postulated can then be related to other reactions. The ion $[Re(NH_2CH_3)_4(NCH_3)Cl]^{2+}$ can be prepared[21] from K_2ReCl_6 and methylamine. When these reagents are mixed with a small amount of water, some hydrogen is evolved, but the conversion to the complex containing deprotonated methylamine is incomlete unless oxygen is admitted. This suggests that the deprotonation is effected by the metal rather than by oxygen, which merely helps to complete the reaction. In the same paper, Shandles and Murmann also report that in pure water the ion $[Re(NH_2CH_3)_4(NCH_3)(OH_2)]^{3+}$ decomposes in a few minutes whereas the ions containing coordinated chloride or hydroxide are more stable. All show high kinetic stability in acidic solution. Thus equation (iii) seems reasonable. The conversion on molybdenum of coordinated amines of type $RR'CHNH_2$ to $RR'CO$ is believed[5] to proceed via a β-elimination rather than direct attack of oxidant on ligand. A similar process is postulated[22] for the ceric ion oxidation of co-ordinated diimines on iron. We suggest that the steps intervening between equation (iii) and the formation of the final product, $Ru(CN)_3 \cdot 3H_2O$, are all relatively fast and may be represented by reactions such as



$$\underset{\mathrm{OH}}{\underset{|}{\mathrm{Ru^{III}}}}\text{–}NH_2CH_3 \rightarrow \underset{\mathrm{H}}{\underset{|}{\mathrm{Ru^{III}}}}\text{–}NH{=}CH_2 + h_2O \qquad \text{(iv)}$$



$$\underset{\mathrm{H}}{\underset{|}{\mathrm{Ru^{III}}}}\text{–}NH{=}CH_2 + H_2O + O_2 \rightarrow \underset{\mathrm{OH}}{\underset{|}{\mathrm{Ru^{III}}}}\text{–}NH{=}CH_2 + H_2O_2 \qquad \text{(v)}$$

The coordinated imine will undergo a similar reaction, while H_2O_2 may also behave as the oxidant in step (v).

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