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Reaction of Nitrosylpentaammineruthenium(II) with Aromatic Aldehydes in Aqueous Base. An Example of Catalyzed Metal Ion Hydrolysis

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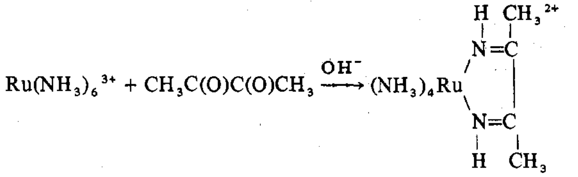
Received March 21, 1978

Evidence is presented that the reaction of $[Ru(NH_3)_5NO]^{3+}$ with several aromatic aldehydes in 0.1 M NaOH forms *trans*-$Ru(NH_3)_4(OH)NO^{2+}$ as the exclusive product, with the aldehyde serving as a catalyst. Electronic spectral data suggest that the reaction takes place via nucleophilic attack of the amido ligand trans to the nitrosyl group at the carbonyl of the aldehyde to form an unstable imine intermediate which hydrolyzes at the metal–nitrogen bond to yield the hydroxo product and quantitatively regenerate the aldehyde.

Introduction

Recent[1-4] studies have shown that deprotonated ammine ligands on ruthenium(III) complexes may act as nucleophiles toward a variety of chemical species such as organic carbonyl compounds, nitric oxide, and ruthenium nitrosyl complexes. The reactions observed were (references match reaction numbers)


(1)

$$Ru(NH_3)_6^{3+} + NO \xrightarrow{OH^-} Ru(NH_3)_5N_2^{2+} \quad (2)$$

$$Ru(NH_3)_6^{3+} + RCHO \xrightarrow[{[O]}]{OH^-} (NH_3)_5RuN{\equiv}CR^{2+} \quad (3)$$

$$Ru(NH_3)_6^{3+} + Ru(NH_3)_5NO^{3+} \xrightarrow{OH^-} (NH_3)_5RuN{\equiv}NRu(NH_3)_5^{4+} \quad (4)$$

In addition, Bottomley[5] has reported that a deprotonated ammine ligand on nitrosylpentaammineruthenium(II) reacts with the nitrosyl group of another molecule of the same species to form a dinitrogenpentaammineruthenium(II) ion and a 3:2 mixture of *cis*- and *trans*-tetraamminehydroxonitrosylruthenium(II) ions.

$$2Ru(NH_3)_5NO^{3+} + 2OH^- \rightarrow Ru(NH_3)_5N_2^{2+} + Ru(NH_3)_4(OH)NO^{2+} + 2H_2O \quad (5)$$

This paper reports on the interaction of $Ru(NH_3)_5NO^{3+}$ with aromatic aldehydes in basic solution as an extension of reactions 3 and 5.

Experimental Section

Chemicals and Equipment. Ruthenium trichloride (Alfa Ventron) and aldehydes (Eastman Organics, Aldrich) were used as received. All other chemicals were reagent grade. Nitrosylpentaammineruthenium(II) trichloride[6] and *trans*-tetraamminehydroxonitrosylruthenium(II) perchlorate[7] were prepared by literature methods and purity was established by comparison of their electronic spectra with those previously reported. Conductivity was measured at 25 °C using a Industrial Instruments Model RC16B2 conductivity bridge.

Reaction between Nitrosylpentaammineruthenium(II) and Benzaldehyde in 0.1 M NaOH. In a typical experiment 0.065 g (204 μmol) of $[Ru(NH_3)_5NO]Cl_3{\cdot}H_2O$ was dissolved in 2 mL of water, 25 μL (245 μmol) of benzaldehyde added, the solution thoroughly mixed and then treated with 2 mL of 0.2 M NaOH. The solution immediately turned a light red and then slowly faded to yellow in about 2 h at room temperature. The solution was normally allowed to stand overnight and then treated with 2 mL of saturated aqueous $NaClO_4$ to produce a bright yellow precipitate, which was washed successively with 95% ethanol and diethyl ether and air-dried (0.049 g yield). The product may also be isolated as a Br^- salt in lower yield by addition of saturated NaBr solution. The benzaldehyde reaction was also carried out at 7 °C. The combined product of several different runs was converted to the halide salts by refluxing with either aqueous HCl or HBr to aid in product identification.

The reaction was also performed using a ruthenium/benzaldehyde molar ratio of 6.6; in one experiment the use of 49 μmol of C_6H_5CHO produced 275 μmol of $[Ru(NH_3)_4(OH)NO](ClO_4)_2$.

In another experiment, after the reaction between $[Ru(NH_3)_5NO]Cl_3$ and C_6H_5CHO (1:1 molar ratio) was complete, $Ru(NH_3)_6Br_3$ (0.105 g, 237 μmol) was added to test for the presence of C_6H_5CHO via reaction 3. The solution immediately turned from yellow to red and then faded upon exposure to atmospheric O_2. Treatment with saturated $NaClO_4$ yielded a bright yellow precipitate.

Reaction between Nitrosylpentaammineruthenium(II) and Hydroxide Ion. In order to provide a reaction blank for the aldehyde systems, the reaction of $[Ru(NH_3)_5NO]Cl_3{\cdot}H_2O$ (0.065 g, 204 μmol) and NaOH (4 mL, 0.1 M) was carried out as described by Bottomley,[5] and products were isolated as described above.

Results

Stoichiometry. A single reaction product (characterized below as $[trans\text{-}Ru(NH_3)_4(OH)(NO)]X_2$) was isolated in yields of 60% or higher (based on Ru content) in all cases (benzaldehyde, *p*-methylbenzaldehyde, and *p*-nitrobenzaldehyde), including the experiment which used a large molar excess of nitrosylruthenium reactant. Further information on the stoichiometry of the $Ru(NH_3)_5NO^{3+}$/aldehyde reaction is provided by an experiment in which $Ru(NH_3)_6Br_3$ was added to the solution after completion of the original reaction. The solid isolated showed a strong IR peak at 2185 cm^{-1}, corresponding to that previously reported for $\nu(C{\equiv}N)$ of $[(NH_3)_5RuNCC_6H_5](ClO_4)_2$, and the solution spectra showed absorption indicative of the presence of $(NH_3)_5RuNCC_6H_5^{2+}$ ion.[3]

Rate Estimates. Visual observations at room temperature of the color changes indicate a half-life of the aldehyde-assisted reactions of about 20 min and of the reaction in base alone of about 3 h. Thus there is roughly a tenfold enhancement of the reaction rate in the presence of equimolar aldehyde.

Characterization of Reaction Products. Infrared Spectra.

0020-1669/78/1317-2819$01.00/0

The infrared spectrum of the product from the aldehyde systems showed typical $\nu(N{\equiv}O)$ peaks at 1890 and 1845 cm^{-1} for the ClO_4^- and Br^- salts, respectively, and sharp new peaks at 3560 cm^{-1} (ClO_4^- salt) or 3485 cm^{-1} (Br^- salt) in the OH stretching region but no indication of a $\nu(C{\equiv}N)$ peak. Furthermore, when the reactions were carried out in the presence of atmospheric oxygen, there was no infrared evidence for the production of a ruthenium(II) nitrile complex as observed in reaction 3. The infrared spectra of products from the reactions at 27 and 7 °C and the reaction with excess Ru complex were identical and were independent of the aromatic aldehyde used.

The infrared spectra of the products obtained from refluxing the initial reaction products with either HCl or HBr showed $\nu(N{\equiv}O)$ peaks at 1880 and 1885 cm^{-1}, respectively, and the peaks in the 3500-cm^{-1} region of the original samples had disappeared.

The infrared evidence is indicative of the formation of *trans*-hydroxotetraammineruthenium(II), $Ru(NH_3)_4(OH)NO^{2+}$, on reaction of aromatic aldehydes with nitrosylpentaammineruthenium(II). Literature values for $\nu(N{\equiv}O)$, 1840 cm^{-1}, and $\nu(OH)$, 3482 cm^{-1}, for *trans*-$[Ru(NH_3)_4(OH)NO]Br_2$ have been reported.[7] The infrared spectral data for the $\nu(N{\equiv}O)$ for the products treated with HCl and HBr correspond to the trans isomers of $[Ru(NH_3)_4ClNO]Cl_2$ and $[Ru(NH_3)_4BrNO]Br_2$, respectively.

Electronic Spectra. The electronic spectra of aqueous solutions of the reaction product in the aldehyde systems exhibited absorption maxima at 429 nm (ϵ 26 M^{-1} cm^{-1}), 328 nm (ϵ 218 M^{-1} cm^{-1}), and 228 nm (ϵ 5600 M^{-1} cm^{-1}) in excellent agreement with literature values[8] for *trans*-$Ru(NH_3)_4(OH)NO_2^+$: 429 nm (ϵ 25 M^{-1} cm^{-1}), 330 nm (ϵ 211 M^{-1} cm^{-1}), 227 nm (ϵ 5750 M^{-1} cm^{-1}). After refluxing the product with either HBr or HCl, the spectra were identical with those reported[8,9] for the trans isomers of $[Ru(NH_3)_4BrNO]Br_2$ and $[Ru(NH_3)_4ClNO]Cl_2$, respectively.

When the reaction was monitored using the visible spectrum, the spectrum immediately after mixing the reactants showed peaks at 340 and 415 nm which decreased within 2 h to yield a final spectrum indicating the presence of *trans*-$[Ru(NH_3)_4(OH)NO]^{2+}$. Neither of these peaks was observed when $Ru(NH_3)_5NO^{3+}$ or C_6H_5CHO was separately treated with 0.1 M NaOH. Evidence for the presence of a reaction intermediate was sought by isolating a solid product shortly after mixing and measuring its infrared spectrum; although no new peaks attributable to an intermediate were observed, the solid on redissolving in 0.1 M NaOH produced a product identical with that obtained in the uninterrupted reaction rather than that obtained from the solid precipitated from a solution containing only $Ru(NH_3)_5NO^{3+}$ and base.

The spectrum of the product obtained from the blank experiments (no aldehyde) showed the expected strong absorption at 221 nm characteristic of $Ru(NH_3)_5N_2^{2+}$.[10]

NMR Spectra. The NMR spectrum of the reaction product (in 18 M H_2SO_4) showed only a single peak for the NH_3 protons at 3.93 ppm with respect to Me_4Si, indicative of the trans isomer. The peak shift compares favorably with those reported in the literature for similar compounds.[11]

Conductivity Experiments. Conductivity measurements made on aqueous solutions of the ClO_4^- salt of the reaction product gave $\lambda = 247 \pm 5$ mhos M^{-1} consistent with a 2:1 type compound as found in measurements of other $[Ru(NH_3)_4LNO]X_2$ compounds.[8]

Discussion

The infrared, electronic, and NMR spectral data demonstrate that the net reaction occurring on treatment of $Ru(NH_3)_5NO^{3+}$ with aromatic aldehydes in 0.1 M NaOH is

$$Ru(NH_3)_5NO^{3+} + OH^- \xrightarrow{RCHO} trans\text{-}Ru(NH_3)_4(OH)(NO)^{2+} + NH_3 \quad (6)$$

$$R = -C_6H_5,\ -p\text{-}C_6H_4NO_2,\ -p\text{-}C_6H_4CH_3$$

However, the reaction is much faster and produces markedly different products than that of $Ru(NH_3)_5NO^{3+}$ in base alone, where the predominant hydroxonitrosyl product is the cis isomer.[5] These facts, along with the spectral changes observed, support an interaction of the aldehyde carbonyl group with a deprotonated ammine ligand analogous to that observed in reaction 3.

In order to verify that the trans isomer was not being formed by the known relatively rapid room temperature isomerization of *cis*-$[Ru(NH_3)_4(OH)NO]^{2+}$ in aqueous base,[5,9] the reaction between $Ru(NH_3)_5NO^{2+}$ and C_6H_5CHO was carried out at a temperature (~7 °C) close to that reported as optimum for reaction 5. Under these conditions, the isomerization of *cis*- to *trans*-$[Ru(NH_3)_4(OH)NO]^{2+}$ is reported[5] to be very slow (e.g., ~10% isomerization in 7 days at 5 °C). When our reaction was carried out for 24 h at 7 °C only the trans isomer of $[Ru(NH_3)_4(OH)NO]^{2+}$ was isolated, indicating that reaction of the aldehyde with the (deprotonated) complex occurs at the trans position.

The above evidence and the observations on the interactions of $Ru(NH_3)_6^{3+}$ with carbonyls[1,3] suggest that the following reactions occur in basic solutions containing $Ru(NH_3)_5NO^{3+}$ ion and aromatic aldehydes

$$Ru(NH_3)_5NO^{3+} + OH^- \rightleftarrows (NH_3)_4(NO)Ru(NH_2)^{2+} + H_2O \quad (7)$$

$$(NH_3)_4(NO)RuNH_2^{2+} + RCHO \rightleftarrows trans\text{-}[(NH_3)_4(NO)RuN(H){=}C(H)R]^{3+} + OH^- \quad (8)$$

$$trans\text{-}[(NH_3)_4(NO)RuN(H){=}C(H)R]^{3+} + OH^- + H_2O \rightarrow trans\text{-}[(NH_3)_4(NO)RuOH]^{2+} + RCHO + NH_3 \quad (9)$$

The pK_a of $Ru(NH_3)_5NO^{3+}$ has been reported[11] to be $\simeq 9$, suggesting extensive deprotonation of one or more NH_3 ligands on $Ru(NH_3)_5NO^{3+}$ to form amido complexes in a rapidly established equilibrium reaction (7). This is followed by a rapid nucleophilic attack (accompanied by the initial color change) by the trans NH_2 on the carbonyl of the aromatic aldehyde, leading to a coordinated imine in a multistep reaction (8). Although the solid isolated at this stage of the reaction did not show a peak assignable to a $\nu(C{=}N)$ vibration, this solid reacts with 0.1 M NaOH to produce *trans*-$[Ru(NH_3)_4(OH)NO]^{2+}$ rather than the mixture of products found in reaction 5. Thus it appears that the intermediate solid isolated contains a small amount of the imino complex.

Further evidence for a ruthenium(II) imine intermediate is the appearance in the reaction solution of a peak at 415 nm (as reported for other ruthenium(II) monoimine species).[3,12] The position of this peak is dependent on phenyl ring substituents, a property characteristic of Ru compounds coordinated to nitriles[13] and imines.[3] In the presence of excess atmospheric oxygen, the imine might be expected to form a ruthenium nitrile species as in reaction 3. It has been suggested that in reaction 3 and in similar reactions[12] the Ru(III) species plays an active role in the formation of the coordinated nitrile and is reduced to Ru(II). This is unlikely for the reaction with the nitrosyl complex, since the ruthenium is considered to be in its +2 oxidation state coordinated to a NO^+ ligand.

The evidence suggests that *trans*-$Ru(NH_3)_4(OH)NO^{2+}$ is formed via reaction 9 by cleavage of the Ru to imine bond, which is weakened by the competition of the imine and NO^+ ligands for the same Ru(II) orbitals. Substitution by OH^- then completes the reaction. Similar reactivity patterns have been found for other Ru(II) complexes in which two ligands capable of back-bonding to Ru(II) are trans to one another.[13,14] The released imine is presumably rapidly hydrolyzed to aldehyde and ammonia in the aqueous basic solution; thus the net reaction corresponds to an aldehyde-catalyzed base hydrolysis of $Ru(NH_3)_5NO^{3+}$.

This catalytic effect was directly established in the reaction containing excess $Ru(NH_3)_5NO^{3+}$ since over 5 mol of *trans*-$[Ru(NH_3)_5(OH)NO](ClO_4)_2$ was produced per mole of C_6H_5CHO present. We also see why attempts to isolate an intermediate yielded a substance that produced only *trans*-$[Ru(NH_3)_4(OH)(NO)]^{2+}$ when redissolved in 0.1 M NaOH, since a small amount of imine intermediate could, when redissolved in 0.1 M OH^-, produce aldehyde to catalyze the base hydrolysis reaction.

The geometrical specificity of the reaction could arise from (1) a significantly larger acidity for the protons on the trans NH_3, (2) a more rapid nucleophilic reaction at the trans position, and/or (3) a much lower rate of hydrolysis of a cis imine intermediate. If (1) is correct, it is difficult to rationalize the formation of both *cis*- and *trans*-$Ru(NH_3)_4(OH)(NO)^{2+}$ in Bottomley's work (especially since the cis → trans conversion is spontaneous[15]). Assuming comparable cis and trans amido concentrations, approach (2) would require a much more rapid attack of aldehyde at the trans position. Bottomley's result would discredit a steric explanation and no readily apparent electronic explanation comes to mind. One might, indeed, expect the trans amido to form a π-bonded ligand less readily than the cis because of "competition" by the $N{\equiv}O^+$ group.

Perhaps the most plausible explanation is that both cis and trans imine intermediates form (at low concentrations and in equilibrium with the starting material) but that only the trans is unstable toward base under the reaction conditions. If this hydrolysis is irreversible because the released imine decomposes to aldehyde and ammonia, the reaction will ultimately produce the trans hydroxy complex quantitatively.

Recent experiments with several aliphatic carbonyl compounds reveal that an entirely different and unexpected reaction occurs; these studies will be reported separately.

Acknowledgment. This research was supported by the Department of Chemistry, Illinois Institute of Technology.

Registry No. $[Ru(NH_3)_5NO]^{3+}$, 37874-79-6; *trans*-$Ru(NH_3)_4(OH)NO^{2+}$, 52720-69-1; benzaldehyde, 100-52-7; *p*-methylbenzaldehyde, 104-87-0; *p*-nitrobenzaldehyde, 555-16-8.

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