[Reprinted from Inorganic Chemistry, 15, 1454 (1976).]

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Reduction of Pyrazine Oxide, Free and Coordinated to Ruthenium(II)

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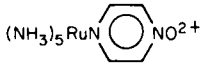
Received October 13, 1975 AIC50739B

Coordination of N_2O to Ru(II) enormously increases the rate of reduction of the oxide by V^{2+} or by Cr^{2+}.[1] A possible explanation of the effect is that Ru(II) assists in the reduction of the coordinated N_2O, with the internal and the external reducing agents cooperating in producing a $2e^-$ reduction of N_2O. On the basis of this hypothesis, it seemed reasonable to suppose that pyrazine oxide when coordinated to Ru(II) would also undergo reduction more rapidly than does free pyrazine oxide. Accordingly, we undertook to study the rate of reduction of both



and

The expected effect was not observed, and as a result our understanding of how Ru(II) enhances the reducibility of N_2O has not been much advanced. Because results we have obtained may nevertheless be of interest in other contexts, we make a brief report of them here.

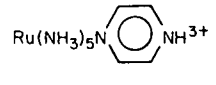
Experimental Section

Pyrazine oxide was prepared following the procedure described by Klein and Berkowitz.[2] The product obtained was recrystallized from benzene and then subjected to analysis. Anal. Calcd: C, 50.0; H, 4.2; N, 29.2. Found: C, 49.4; H, 4.23; N, 29.3. The ir and uv spectra agreed well with those described.[2]

The ion $Ru(NH_3)_5C_4H_4N_2O^{2+}$ was prepared by mixing $Ru(NH_3)_5OH_2^{2+}$ with pyrazine oxide, the former in 10% excess, under an atmosphere of argon. After complexation was complete, saturated sodium bromide was added. The solid was collected, washed, and dried. Anal. Calcd for $[Ru(NH_3)_5C_4H_4N_2O]Br_2$: C, 10.87; N, 22.18; H, 4.33; Br, 36.14. Found: C, 10.56; N, 21.97; H, 4.28; Br, 36.98.

Solutions containing V(II) and Cr(II) were prepared by standard procedures.

The spectrophotometric method was used in determining reaction rates. In all cases, experiments were done under pseudo-first-order conditions, with the reducing agent being used in excess. For V(II) in reaction with uncomplexed ligand, measurements were made at 214 nm; this wavelength is at a band maximum for pyrazine oxide, the product pyrazine showing much weaker absorption. Advantage was taken of the $\pi^* \leftarrow \pi d$ charge-transfer transition in measuring the rate of reduction of the complex of pyrazine oxide with Ru(II). The band maxima for the reactant complex and the product[3]



in acid solution coincide (λ 527 nm) but there is enough difference in the extinction coefficients to make it possible to follow the reaction using light in the visible region of the spectrum. With Cr^{2+} as reductant, reaction is too rapid for the rate to be measured by ordinary

Table I. Rate of Reduction of Pyrazine Oxide and of Its Complex with Pentaammineruthenium(II) by $V^{2+}(aq)$[a]

Oxidizing agent	k, M^{-1} s^{-1},[b] at 25.0 °C	19.9 °C	14.8 °C	9.8 °C
Free ligand	2.29	1.79	1.36	1.03[c]
Complex	0.204	0.159	0.117	0.088[d]

[a] $\mu = 0.10$; oxidizing agent at 6.5×10^{-5} M. [b] Each experiment is the mean of three in which $[V^{2+}(aq)]$ covers the range of (ca. 9.0–4.3) $\times 10^{-4}$ M, and $[H^+]$, the range of (ca. 5.0–2.3) $\times 10^{-2}$ M. There is no trend in the values of k over this range. The average deviation from the mean is ca. 2%. [c] $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ from Eyring plots are 8.1 ± 0.5 kcal/mol and −18 ± 2 cal mol^{-1} deg^{-1}. [d] $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 10.0 ± 0.5 kcal/mol and −17 ± 2 cal deg^{-1} mol^{-1}.

spectrophotometric means, and a stopped-flow apparatus was used for this system.

Under our conditions with V(II) as reductant, reaction is effectively arrested when the ligand is reduced to pyrazine, whether pyrazine oxide is complexed or uncomplexed. The net change in the first stage with V(II) in excess then is

$$2V^{2+} + C_4H_4N_2O + 2H^+ = 2V^{3+} + C_4H_4N_2 + H_2O$$

With Cr(II) as reductant, when the ligand is complexed, reaction again is arrested at the pyrazine level of oxidation, but with uncomplexed ligand, reduction proceeds beyond the pyrazine state. The chemistry of this system was not investigated in any detail and the only observation of note made in the study is that there is a great decrease in the reactivity of pyrazine toward Cr^{2+} when the ligand is complexed, amounting to a factor of at least 10^{-3}. With Cr^{2+} at 0.01 M, there is no detectable reaction with $Ru(NH_3)_5C_4H_4N_2^{2+}$ in 10 min, but with uncomplexed ligand, reaction appears to be complete on mixing ($t_{1/2} < 5$ s).[4]

Results

The large bathochromic shift in the $\pi^* \leftarrow \pi d$ transition (from 472 to 527 nm) caused by adding O to the remote end of pyrazine when this is coordinated to Ru(II) has already been noted—the shift in fact is as large as that produced by H^+. The extinction coefficient at the band maximum is 1.4×10^4 M^{-1} cm^{-1}. The infrared spectrum is also of interest in characterizing pyrazine oxide when it is coordinated to ruthenium(II). Measurements were made on $[Ru(NH_3)_5C_4H_4N_2O]Br_2$. The region of the spectrum in which the N–O stretching frequency is expected to appear shows bands at 1293 and 1258 cm^{-1} there possibly being weak shoulders at 1286 and 1265 cm^{-1}. The band at 1258 cm^{-1} is most likely the N–O stretch while that at 1293 cm^{-1} can be assigned to $\delta(NH_3)$.

The results of the measurements of the rate of reduction by V^{2+} of pyrazine oxide as free ligand and in the pentaammineruthenium(II) complex are summarized in Table I.

With Cr^{2+} as reductant, the stopped-flow apparatus[5] was used for the measurements. Experiments at 25.0 °C in $NaClO_4$–$HClO_4$ ($\mu = 0.11$, $[H^+] = 5.7 \times 10^{-2}$ M) yielded for k the values 13.8, 13.2, 12.8, and 13.8 M^{-1} s^{-1} for reduction of the coordinated oxide. Owing to complications arising from the further reduction by Cr^{2+} of the intermediate product pyrazine, we have no estimate of the rate at which free pyrazine oxide is reduced by Cr^{2+}.

Comments

When pyrazine oxide coordinates to $Ru(NH_3)_5^{2+}$, the N–O stretching frequency is reduced from 1313 cm^{-1} for the free ligand[5] to 1258 cm^{-1} implying then that πd–π^* back-bonding is antibonding for the N–O interaction. Even if the assignments of the N–O stretch and $\delta(NH_3)$ are interchanged, this conclusion still follows. However, though the force constant for the NO bond is decreased, the reduction by V^{2+} of the coordinated oxide, which does involve N–O bond rupture, is not facilitated. In fact, at 25 °C the rate of reduction of the coordinated ligand is less than that of the free, but in view of the somewhat different value of $\Delta H^{\ddagger}$ for the two reactions, the rates will reverse at sufficiently high temperature.

It is, of course, not necessary that a decrease in the N–O force constant will result in an increase in rate of reduction. In assessing the effect of coordination, we need to take account of the stability changes for the whole system rather than focusing on the N–O bond. The shift in the $\pi^* \leftarrow \pi d$ transition, from 472 nm for coordinated pyrazine to 527 nm for pyrazine oxide, shows that there is a considerable increase in the back-bonding interaction when coordinated pyrazine is transformed to the oxide. This extra stabilization is lost on reduction, and this loss of stability could well be reflected at least partially in the activated complex for the reaction.

For reactions in which substitution on $V(H_2O)_6^{2+}$ by a ligand carried in a complex of net charge 2+ is rate determining, specific rates of the order of 10 M^{-1} s^{-1} are observed.[7,8] Even though the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ recorded for the reaction of $V(H_2O)_6^{2+}$ with $Ru(NH_3)_5C_4H_4N_2O^{2+}$ are similar to those observed for the reactions mentioned in ref 7 and 8, the specific rate at 25 °C of 0.20 M^{-1} s^{-1} recorded for our system is so low that, if an inner-sphere precursor complex is formed, it can be assumed that the complex is substantially at equilibrium with the reactants and that the slow step involves internal electron transfer or some other mode of decomposition of the inner-sphere complex. For the reaction of $V(H_2O)_6^{2+}$ with the free ligand, the kinetic parameters are so different from those observed for the exchange of water between $V(H_2O)^{2+}$ and solvent[9] that it again seems unlikely that substitution is rate determining. Here only the values of $\Delta H^{\ddagger}$ are directly comparable owing to the difference in molecularity in the processes; $\Delta H^{\ddagger}$ for water exchange is 16.4 ± 0.6 kcal/mol while for the reduction of pyrazine oxide by $V(H_2O)^{2+}$ it is 8.1 ± 0.5 kcal/mol. Thus it seems safe to conclude that the comparison of rates in our systems is not vitiated because the rate of one or other reaction is controlled by substitution.

The stabilization of pyrazine when it is coordinated to Ru(II) to reduction by Cr^{2+} is also worthy of note. Here again the stabilization can be attributed to back-bonding, this stabilization being lost when pyrazine is reduced.

No change in the rate of reduction of the free ligand or of the complex was registered over the range of acidity which was covered by our experiments. In view of the fact that protonated pyridine oxide has a pK_a value[10] of less than 1, it is unlikely that pyrazine oxide is significantly protonated at the acidities used in our studies.

Our work on these systems is admittedly incomplete, and a serious shortcoming in this respect is that the nature of vanadium and chromium products was not established. In the presence of excess V(II), the final vanadium product will be V(III), but VO^{2+}, if it were formed as an intermediate,[11] should be identifiable in the present system at lower acidity. A $2e^-$ change in oxidizing Cr^{2+} would be expected to produce the chromium(III) "dimer", which can readily be identified by cation-exchange techniques.

Acknowledgment. Fellowship support of M. A. Blesa by the Conseja Nacional de Investigaciones of Argentina and partial support of the research under GM13868 are gratefully acknowledged.

Registry No. Pyrazine oxide, 2423-65-6; $[Ru(NH_3)_5C_4H_4N_2O]Br_2$, 58409-48-6; $V(H_2O)_6^{2+}$, 15696-18-1; chromium, 7440-47-3.

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