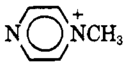
Evidence for an Unusual Association between Two Cations in Aqueous Solution

Sir:

The heterocycle *N*-methylpyrazinium ion **1** (MPz^+) in aqueous solution substitutes readily for water in the



1

inner coordination sphere of the pentaammineaquoruthenium(II) ion to form the cation pentaammine, *N*-methylpyraziniumruthenium(II).[1] To determine whether the remarkable stability of the product ion would be manifested in the substitution process, we have investigated the kinetics of the reaction. Our evidence indicates that an associative intermediate of surprising stability is formed. The existence of the new species appears to us sufficiently novel to warrant this report. Also of interest is the pronounced pH dependence of the rate of the overall reaction, indicating substantial protonation of the intermediate below pH 3.

The kinetics of the reaction were studied in aqueous *p*-toluenesulfonate solution at $\mu = 1.00$ *M* in the temperature range 11-37° using an argon atmosphere. $[Ru(NH_3)_5Cl]Cl_2$[2] (approximately $10^{-4} M$) was treated in solution with zinc amalgam for 20 min to form $[Ru(NH_3)_5H_2O]^{2+}$[3] and injected into the deaerated ligand solution (10^{-3}–0.4 *M*) contained in a sealed spectrophotometric cell. The formation of the complex was followed at a constant temperature at 540 nm.

The observed pseudo-first-order rate constant (k_{obsd}) showed an inverse dependence in $[H^+]$ as is reported in Figure 1. An expanded plot in the pH 1-2 interval yielded a straight line which obeys the equation

$$k_{obsd} = 2.1 \times 10^{-4} + 2.7 \times 10^{-6} \times 1/[H^+] \quad (1)$$

In the region beyond pH 3.5 (to pH 5) the $[H^+]$ dependence practically ceased. Besides influencing the rate of reaction, the hydrogen ion concentration also affected the stoichiometry: the yield of the product complex decreased considerably with increasing $[H^+]$ in the pH 1-3 interval. A 100% yield (based on initial ruthenium(II) reducing power) was attained at pH 3.5 and above.

The dependence of k_{obsd} on the ligand concentration showed the saturation behavior represented in Figure 2A (pH 4.5). The study was repeated at pH 3.0 and 1.0 (curve shown in Figure 2B) and a shift of the saturation point to lower concentrations of the ligand and to lower values of k_{obsd} was obtained as follows (pH, saturation point, limiting k_{obsd}): 4.5, 0.35 *M*, 2.4×10^{-3} sec^{-1}; 3.0, 0.06 *M*, 1.0×10^{-3} sec^{-1}; 1.0, 0.03 *M*, 2.2×10^{-4} sec^{-1}.

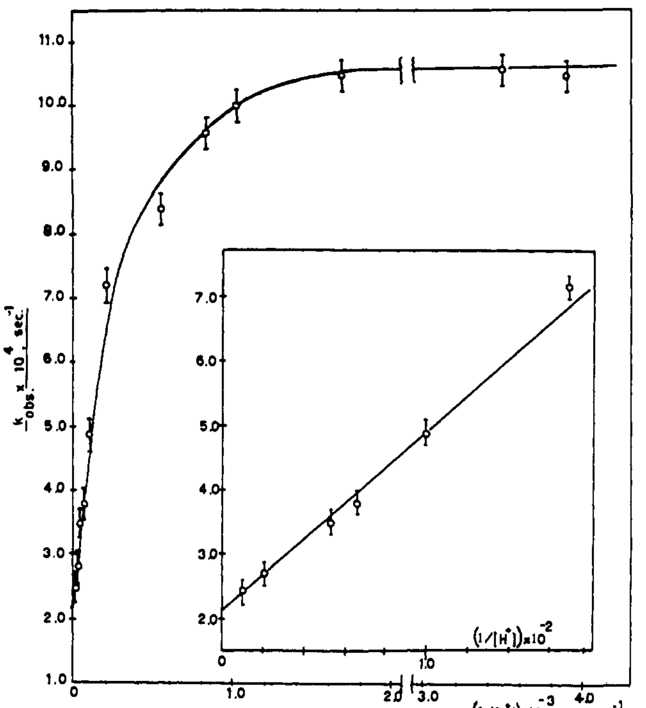


Figure 1. Dependence of k_{obsd} on the inverse hydrogen ion concentration. Inset: an expanded plot of the initial points. $[MPz^+] = 0.050$ *M*, $[Ru(NH_3)_5OH_2]^{2+} \approx 10^{-4}$ *M*, 30°, $\mu = 1.00$ (lithium *p*-toluenesulfonate).

The occurrence of saturation suggests the formation of an intermediate complex. The pH-dependent behavior indicates association with protons in an equilibrium process leading to another, less reactive species. Thus, both the inverse hydrogen ion dependence and the observed shift of the saturation point can be understood. We have excluded the possibility of protonation of the reactants because of their low basicities.[4]

The decreasing yield with increasing $[H^+]$ is probably due to redox processes which take place in the protonated intermediate leading to the oxidation of ruthenium(II). Ligand reduction at low pH was also encountered by Shepherd[5] as a side reaction to ruthenium(II) complexation.

Based on the observations above we suggest the mechanism of eq I, for which k_{obsd} is expressed in eq 2.

$$\begin{tikzcd}
{[(NH_3)_5RuOH_2]^{2+} + MPz^+} \arrow[r, shift left, "K"] & I \arrow[l, shift left] \arrow[r, "k_1"] \arrow[d, shift right, "{K', +H^+}"'] & {[(NH_3)_5RuMPz]^{3+} + H_2O} \\
 & I' \arrow[u, shift right, "-H^+"'] \arrow[r, "k_2"] & \text{redox products}
\end{tikzcd} \quad (I)$$

$$k_{obsd} = \frac{(k_1K + k_2KK'[H^+])[MPz^+]}{1 + K[MPz^+] + KK'[MPz^+][H^+]} \quad (2)$$

One can see that saturation will be reached when the ligand-dependent terms in the denominator of expression 2 are large. Working above the kinetic saturation point in $[MPz^+]$ at pH 4.5, where the $[H^+]$ dependence

---

[1] The product ion, $[Ru(NH_3)_5MPz^{3+}]$, was first prepared by C. Creutz, Ph.D. Dissertation, Stanford University, 1970. We isolated $[Ru(NH_3)_5MPz]Br_3 \cdot 2H_2O$. *Anal.* Calcd: C, 10.7; N, 17.6; Br, 43.0. Found: C, 10.5; N, 17.9; Br, 42.8 (Stanford Microanalytical Laboratory). The complex exhibits a large bathochromic shift (λ_{max} = 540 nm, $\epsilon = 1.6 \times 10^4$ M^{-1} cm^{-1}) and a high oxidation potential ($E° = -0.89$ V, Latimer convention) compared with the pentaammine-pyrazine complex (472 nm, -0.51 V) and the aquopentaammine complex ($E° = -0.16$ V), suggesting a very large backbonding stabilization.

[2] L. H. Vogt, Jr., J. L. Katz, and S. E. Wiberly, *Inorg. Chem.*, 4, 1157 (1965).

[3] Reduction by zinc–mercury amalgam of solutions of $[Ru(NH_3)_5Cl^{2+}]$ gave $[Ru(NH_3)_5OH_2]^{2+}$ since the ion $[Ru(NH_3)_5Cl]^+$, which is presumably formed initially, is rapidly aquated: T. J. Meyer and H. Taube, *ibid.*, 7, 2369 (1968); J. F. Endicott and H. Taube, *J. Amer. Chem. Soc.*, 84, 4984 (1962).

[4] Protonation of a ruthenium(II) d orbital has been postulated to occur only to a catalytically important extent [P. C. Ford, D. P. Rudd, R. Gaunder, and H. Taube, *ibid.*, 90, 1187 (1968)]. The pK_a of $HMPz^{2+}$ must be much smaller than that of pyrazinium ion ($pK_a = 0.65$).

[5] R. E. Shepherd, Ph.D. Dissertation, Stanford University, 1971.

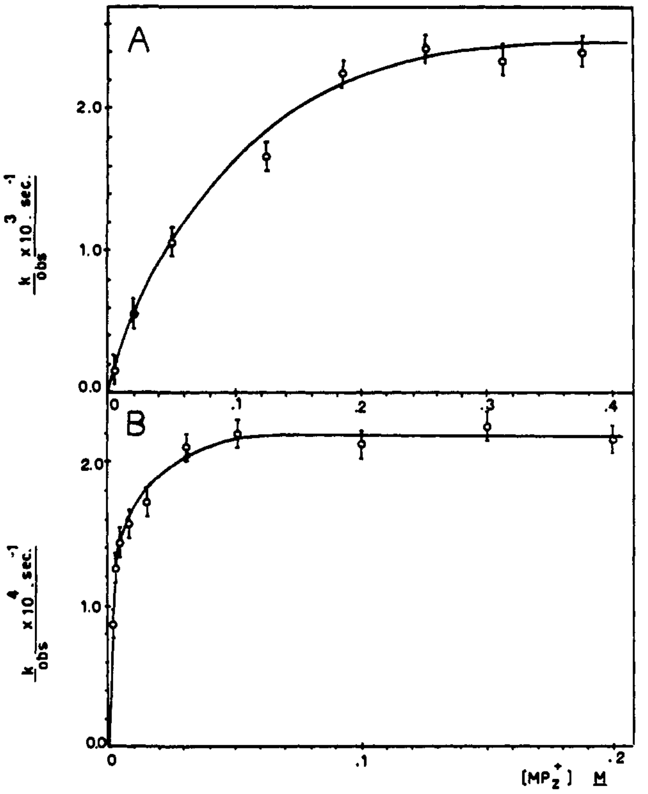


Figure 2. Dependence of k_{obsd} on the ligand concentration. Part A: dependence studied at pH 4.5, 30°, μ = 1.00, $[Ru(NH_3)_5OH_2]^{2+} = 0.5 \times 10^{-4}$ *M*. Part B: pH 1.0, 30°, μ = 1.00 (lithium *p*-toluenesulfonate), $[Ru(NH_3)_5OH_2]^{2+} = 1.0 \times 10^{-4}$ *M*.

virtually disappears, the observed rate constant reduces simply to k_1. Experimentally, $k_1 = 2.4 \times 10^{-3}$ sec^{-1}.

At high [H$^+$] the term $KK'[MPz^+][H^+]$ prevails in the denominator and expression 2 becomes

$$k_{obsd} = k_2 + k_1/K'[H^+] \qquad (3)$$

Comparing with expression 1 and using the previously obtained k_1 value we calculate $k_2 = 2.1 \times 10^{-4}$ sec^{-1} and $K' = 8.9 \times 10^2$ M^{-1}. By substituting these values in expression 2, an association constant K = 16 M^{-1} was found. The curves in Figure 2 can be generated substituting in expression 2 the values given for k_1, k_2, K, and K'.

According to the mechanism given above the quotient of the product concentration, [P], over [R], the concentration of ruthenium(II) lost by a redox process, would be given by

$$[P]/[R] = k_1/k_2K'[H^+] \qquad (4)$$

On studying the variation of [P]/[R] with [H$^+$] and assuming $[R] = [Ru(II)_{total}] - [P]$ we found excellent linear dependence on the inverse of [H$^+$], expressed by eq 5.

$$[P]/[R] = 1.3 \times 10^{-2}/[H^+] \qquad (5)$$

Comparing expressions 5 and 4, and using for k_1 and k_2 our previous values, we calculated $K' = 8.7 \times 10^2$ M^{-1} in agreement with the result found using eq 3.

Independent evidence for the existence of the intermediate was found in a competitive kinetic study at pH 4 based on the expectation that intermediate formation would reduce the free concentration of aquopentaammineruthenium(II) by a factor $1/(1 + K[MPz^+])$. At pH 4.0, T = 30°, k_{obsd} for the reaction of 6.0×10^{-5} *M* aquopentaammineruthenium(II) with aqueous pyrazine (0.100 *M*) was 9.0×10^{-3} sec^{-1}. In the presence of the added component 0.25 *M* *N*-methylpyrazinium ion, k_{obsd} was 4.9×10^{-3} sec^{-1} (measured at 493 nm, the isosbestic point for the two products). Although the presence of *N*-methylpyrazinium provides an additional path for consumption of reactant Ru(II), the rate of reaction is actually diminished by the presence of that ligand. From these measured rate constants the value of the formation constant for the intermediate is 10 M^{-1} while that found in the previous considerations was 16 M^{-1}. The difference is outside experimental error and suggests that the intermediate has some reactivity with respect to pyrazine.[6]

A temperature dependence study in the 11–37° range at pH 4.5 before and after kinetic saturation in the ligand concentration gave the activation parameters for the step k_1, $\Delta H^{\neq} = 18.4 \pm 0.5$ kcal/mol and $\Delta S^{\neq} = -10 \pm 2$ eu, and for the equilibrium process K, the values $\Delta H = -5.7 \pm 1$ kcal/mol and $\Delta S = -17 \pm 3$ eu.

The entropy change associated with formation of the intermediate is, as expected, unfavorable because of decreasing entropy of solvation. We suggest that the enthalpy of complexation, −5.7 kcal/mol, is largely due to the interaction of filled ruthenium(II) t_{2g} orbitals with low-lying acceptor orbitals of the ligand. This interpretation is consistent with the fact that in the product complex the t_{2g}–π^* interaction is unusually strong.[1,7]

---

(6) The observed distribution of products gave a clear indication that the reactivity of the intermediate is affected by the added heterocycle, and this effect, as well as other properties of the intermediate, is under investigation in this laboratory. Nevertheless, the competitive experiment shows unequivocally that the presence of *N*-methylpyrazinium ion markedly retards the rate of Ru(II) complexation.

(7) The experimental results do not distinguish between an intermediate of the "inner" or of the "outer-sphere" type. The authors, seeing a similarity between the activation enthalpy measured for the k_1 step and values of $\Delta H^{\neq}$ which have been measured for processes in which water in the ion $[Ru(NH_3)_5OH_2^{2+}]$ is replaced by various N heterocycles,[5] favor the interpretation that the interaction is of the "outer-sphere" type.

(8) The authors gratefully acknowledge financial support from the following: the Conselho National de Pesquisas, the Fundação de Amparo a Pesquisa do Estado de Sao Paulo (H.E.T., Predoctoral Fellowship), the Atlantic Petroleum Company of Brasil, the Agency of International Development, the National Science Foundation, the National Academy of Sciences and the Atlantic Richfield Corporation of the U. S. Also acknowledged gratefully are the aid and encouragement of Professors Ernesto Giesbrecht and Henry Taube.

Henrique E. Toma, John M. Malin*[8]
Instituto de Química, Universidade de São Paulo
São Paulo, Brazil

Received January 25, 1972

Triplet Energies, Reduction Potentials, and Ionization Potentials in Carbonyl–Donor Partial Charge-Transfer Interactions. I

Sir:

Charge-transfer (CT) type complexes[1–12] have been proposed as intermediates in the photoreduction and

---

(1) S. G. Cohen and H. M. Chao, *J. Amer. Chem. Soc.*, **90**, 165 (1968).

(2) S. G. Cohen and J. I. Cohen, *ibid.*, **89**, 164 (1967); *J. Phys. Chem.*, **72**, 3782 (1968).

(3) S. G. Cohen and N. Stein, *J. Amer. Chem. Soc.*, **91**, 3690 (1969).

(4) S. G. Cohen and A. D. Litt, *Tetrahedron Lett.*, 837 (1970).