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Complexation of Hexaaquoiron(III) with Highly Charged Ligands: Kinetics of Conversion of outer- into inner-Sphere Complexes

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The introduction of fast mixing and relaxation techniques has made possible to establish that complex formation occurs through discrete steps which are characterized by the presence of outer-sphere (or solvent separated) and inner-sphere (or contact) complexes in equilibrium with the free ions. According to Eigen and Tamm [1] this can be depicted by the scheme (1)

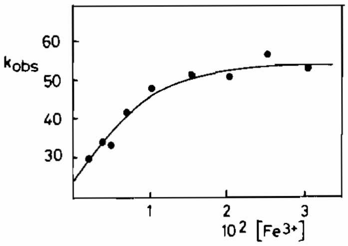
$$\mathrm{M(H_2O)_6 + L} \underset{}{\overset{K_{os}}{\rightleftharpoons}} \mathrm{M(H_2O)_6, L}$$

outer-sphere

$$\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{M(H_2O)_5L + L} \qquad (1)$$

inner-sphere

where K_{os} is the equilibrium constant for the formation of the outer-sphere complex, k_1 and k_{-1} are rate constants for the step of conversion of the outer- into the corresponding inner-sphere complex and *vice-versa.* For the above mechanism the observe first-order rate constant is [2]



$$k_{obs} = \frac{K_{os}k_1[M]}{1 + K_{os}[M]} + k_{-1} \qquad (2)$$

provided that $[M] >> [L]$.

In the majority of the investigated systems is $K_{os}[M] << 1$ and eqn. (2) is reduced to [2, 3]

$$k_{obs} = K_{os}k_1[M] + k_{-1} \qquad (3)$$

The only way to obtain k_1 is to estimate K_{os} with the help of appropriate equations which suffer of the disadvantage of introducing arbitrary assumptions about the distance apart of the ions in the outer-sphere complex [4].

The systems investigated in the present study $Fe^{3+}/Fe(CN)_6^{3-}$ and $Fe^{3+}/Co(CN)_6^{3-}$ are characterized by high values of K_{os} and represent two rare cases in which the rate law hold in the full form (eqn. 2). This is shown in Fig. 1 where, for the system $Fe^{3+}/Co(CN)_6^{3-}$ at ionic strength 0.3 M, the rate levels off at $M > 0.02$ M. Values of k_1, k_{-1} and K_{os} are reported in Table I (Temperature 25 °C.) The experimental K_{os} agree with the values calculated with the Fuoss [5] equation (a = 6 Å). The values of k_1 must correspond to the rate of water exchange at the metal ion (k_{H_2O}) if the interchange mechanism is dissociative [1]. In our cases k_1 are about one order of magnitude lower than k_{H_2O} suggesting that complexations of iron(III) are associative in nature and the solvent molecules are retained in the transition state.

References

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TABLE I.

Ligand	k_1 (sec^{-1})	k_{-1} (sec^{-1})	K_{os} (M^{-1})	$K_{os\ calcd}$ (M^{-1})
$Fe(CN)_6^{3-}$	30	23	100	90
$Co(CN)_6^{3-}$	50	24	70	90

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Solvent Effects in Substitution Reactions at Square Planar Formazan Complexes of Palladium(II) and Platinum(II)

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The kinetics of the reaction

$$\mathrm{FoMX + Y \rightarrow FoMY + X}$$

are reported. Here M = Pd, Pt; X = NH_3 and pyridine; Y = triphenylphosphine, thiourea and thiocyanate; Fo is the tridentate 1-(2-hydroxyphenyl)-3,5-diphenylformazanato ion. The reaction was studied in the solvents propylenecarbonate, methanol, acetonitrile, acetone, DMSO, DMF and 1,4-dioxane.

Generally a two-term rate-law was found:

$$\mathrm{Rate} = k_1[\mathrm{FoMX}] + k_2[\mathrm{FoMX}][\mathrm{Y}]$$

Activation parameters for one system in different solvents were related in an isokinetic relationship, indicating a similar intrinsic mechanism in all solvents studied. A thorough analysis was performed on the k_2 values by way of a separation of solvent effects on initial and transition states. The transfer chemical potentials of initial and transition states were found to follow each other closely, except for solvents of high Gutmann donor number (DMSO, DMF) or acceptor number (methanol). Therefore, the transfer Gibbs free energies of activation per system were tentatively fitted to the two-parameter equation:

$$\delta_m \Delta G^{\ddagger} = p_0 + p_1 \cdot \Delta \mathrm{DN} + p_2 \cdot \Delta \mathrm{AN}$$

In all cases the multiple correlation coefficients had a value over 0.9. This result can be interpreted as an indication for the importance of donor and acceptor interaction at the reative site in the formation of the transition state.

The model was checked by recording the ^{195}Pt NMR spectra of the $FoPtNH_3$ complex in the solvents used for the kinetics. With only one exception the systems that gave a measurable signal showed a linear correlation between chemical shift and donor number.

Solvent Effects on Ligand Exchange between Two Different Pd(II) Organometallic Complexes

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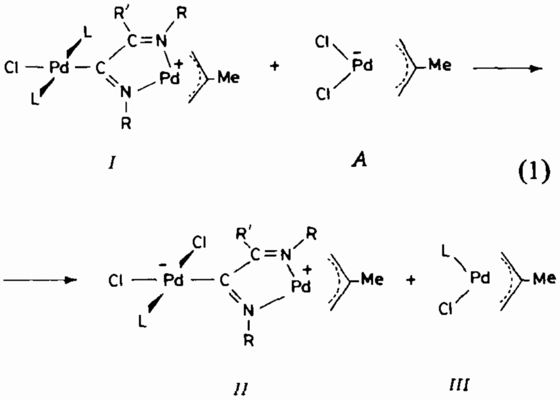
We have studied the mechanism of the following transfer of ligands between Pd(II) metal centers of different complex moieties:



(1)

(L = PPh_3, $AsPh_3$; R = p-C_6H_4OMe; R' = H, Me)

at various temperatures and ionic strengths in different solvents.

The pseudo-first order rate constants for the disappearance of *I* fit the complex rate law (2):

$$k_{obs} = k_1 + \frac{k_2 K_e [A]}{1 + K_e [A]} \qquad (2)$$

indicating a formal mechanism of the type (3):

$$\begin{tikzcd} I + A \arrow[r, shift left, "K_e"] \arrow[dr, "k_1"'] & \{I \cdots A\} \arrow[l, shift left] \arrow[r, "k_2"] & II + III \\ & \{I^*\} \arrow[ur, "+A", "\text{fast}"'] & \end{tikzcd} \qquad (3)$$

The pre-equilibrium step (K_e) is shown by ^{1}H NMR and electronic spectra to be the formation of an associated species, in which a fast $\eta^3 \rightleftharpoons \eta^1$ conversion of the allyl of *I* occurs; this is followed by a