Kinetics of Chelate Formation between Lanthanum(III) and 4-(2-Pyridylazo)-resorcinol

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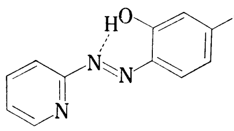
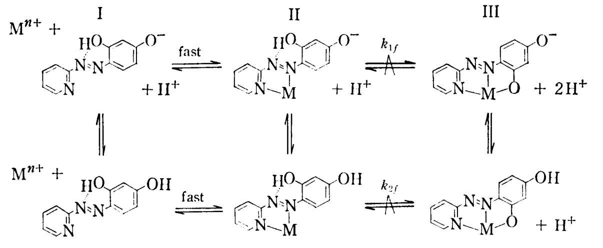
In connection with the slowest liberation of the proton in aqueous solutions from the heavily blocked internal hydrogen bond in a series of *o*-hydroxyazo dyes as reported by Eigen *et al.*,[1,2] we report here some interesting kinetic effects of the fast formation of metal chelate ring on the rate of subsequent protolytic dissociation of an inert hydrogen bond in a ligand molecule of similar structure.



PAR

4-(2-Pyridylazo)-resorcinol (PAR)[3,4] was chosen as a typical ligand of this type requiring a prior rupture of the internal hydrogen bridge between the *o*-hydroxyl and the azo-group to form a final metal chelate of terdentate structure.[5] With the metal ions, for which the very fast substitution of the coordination water would be expected, the overall rate of chelate formation of such terdentate ligands as PAR would thus be determined by the slow rupture of the hydrogen bond. The reaction scheme is shown as follows:



The present communication deals with the reaction of PAR with lanthanum(III) ion, the first member of the terpositive lanthanoids, which show quite regular change in ionic radii and substitute very rapidly their coordination water.[6,7] The continuous variation method showed a 1:1 complex formation. The apparent stability constant was spectrophotometrically determined to be $K=[\mathrm{LaPAR}][\mathrm{H}]/[\mathrm{La}][\mathrm{HPAR}]=10^{-3}$—$10^{-2}$ at about pH 5.9.

The rate constants for the dissociation and the recombination of the internal hydrogen bond of the ligand PAR were determined by the temperature-jump method to be $k_D=6.4\times10^5$ M^{-1}sec^{-1} and $k_R=6.2\times10^3$ sec^{-1}, respectively, at 25°C and ionic strength 0.1 ($NaClO_4$). Values of activation energy for k_D and k_R were 2.5 and 5.9 kcal·mol^{-1}, respectively.

The rate of formation of the La(III)-PAR complex was measured by the stopped-flow method in the pH range 4.2—6.2 buffered with hexamine and at 505 nm, the λ_{max} of the complex III. The rate was found to be dependent on the hydrogen ion concentrations and independent of the metal ion concentrations for the excess of lanthanum(III), suggesting the overall reaction rates determined by the slow rupture of the hydrogen bond in the steps II$\rightleftharpoons$III and II'$\rightleftharpoons$III'.

The rate constants $k_{1f}=38$ sec^{-1} and $k_{2f}=430$ sec^{-1} were obtained on the assumption that the hydrogen-bridged species II and II' are inert as compared with the fully-chelated metal complexes III and III'. Lanthanum(III) reacts with the ligand PAR *ca.* 10^{-6} times as slow as with any ligands containing no internal hydrogen bond. The slowness in rupture of the internal hydrogen bond in the metal complex formation as compared with that in the protolysis of the free ligand can be attributed to the increased inertness of the hydrogen bond in the partly-chelated intermediates II and II' containing two fused chelate rings.

Activation energy of the complex formation strongly suggests that the intermediates II and II' retain the hydrogen-bonded structure of the ligand molecules and the rupture of this bond in turn constitutes the rate-determining step to form the final products III and III'. From a comparison of the rate constants of the hydrogen-bond dissociation in the ligand PAR with those of the metal complex formation, the activation energy was calculated to be 8.3 kcal·mol^{-1}, and experimentally found to be 8.1 kcal·mol^{-1}. Both values are in good agreement. Therefore, it would be reasonable to assume the given two-step mechanism involving the very fast metal chelate ring formation on the heterocyclic nitrogen atom and one of the azo-nitrogen atoms, and the subsequent slow chelate ring formation on the *o*-hydroxyl oxygen and other azo-nitrogen atoms to form the final terdentate structure with fused metal chelate rings.

The hydrogen-bonded ligand structure of PAR seriously affects the formation rate and the stability of the metal complexes.[8] The series of rare earth metal ions may reveal the influences of size and coordination requirements of the metal ions on the reaction mechanisms.

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[5] A terdentate structure of the chelate is also predicted for PAR as demonstrated by the X-ray analysis of the Cu(II) complex of a similar ligand PAN [1-(2-pyridylazo)-2-naphthol]; *cf.* S. Ooi, D. Garter, and Q. Fernando, *Chem. Commun.*, **1967**, 1301.

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[8] Slow complex formation was also observed by the present authors between PAR and Cu(II), a d^9 element.