Correspondence

Mechanisms of Racemization of $M(phen)_3^{2+}$ Ions

AIC60316P

Sir:

A few years ago Sutter and Hunt[1] reported that $Cr(phen)_3^{2+}$ (phen = 1,10-phenanthroline) reacted with $(+)_D$-$Co(phen)_3^{3+}$ to yield $(-)_D$-$Cr(phen)_3^{3+}$ and that when $(-)_D$-$Co(phen)_3^{3+}$ was the reactant $(+)_D$-$Cr(phen)_3^{3+}$ resulted. There was thus indicated a substantial (84%) stereospecificity in this outer-sphere redox reaction. The observations demanded additionally that the (rapid) redox reaction must be much slower than the inversion of $Cr(phen)_3^{2+}$, so as to allow the optical form of $Cr(phen)_3^{2+}$ which is oxidized more rapidly by $Co(phen)_3^{3+}$ to be continuously regenerated. This required a racemization half-life << 1 s for the optical forms of $Cr(phen)_3^{2+}$.

Some results we obtained at about the same time indicated a half-time for racemization of $(+)_D$-$Cr(phen)_3^{2+}$ of some 5–7 s at 25 °C. This observation was obviously incompatible with that of asymmetric induction,[1] and we concluded that there was some artifact in our work. However, recently a number of outer-sphere redox reactions involving an optically active cobalt(II) or cobalt(III) complex as one of the partners have been examined.[2] In no case was asymmetric induction achieved, a finding consistent with earlier kinetic studies of related systems.[3] The reaction of $(+)_D$-$Co(phen)_3^{3+}$ with $Cr(phen)_3^{2+}$ was reexamined, and the previous observation[1] of the production of $(-)_D$-$Cr(phen)_3^{3+}$ from $Cr(phen)_3^{2+}$ could not be confirmed.[2] This development prompts us to report our findings on the configurational lability of the $Cr(phen)_3^{2+}$ ion, as well as supplement our previous findings[4] with $Co(phen)_3^{2+}$ ion.

Four milliliters of 1.0 mM $(+)$-$Cr(phen)_3^{3+}$ (ref 5) was added from a syringe through a serum cap to a stirred flask containing 16 ml of 5 mM $Cr(dipy)_3^{2+}$. After a predetermined time, the resultant $Cr(phen)_3^{2+}$ was rapidly oxidized back to $Cr(phen)_3^{3+}$ by adding 7 ml of 30 mM $Fe(dipy)_3^{3+}$ ion.[6] The specific rotations of the Cr(III) complex before and after[7] the redox cycle reflected the extent of racemization of the Cr(II) phenanthroline complex during its existence. A number of separate experiments were carried out in which the lifetime of the Cr(II) complex was varied. A good deal of scattering was observed in the resultant log (optical retention) vs. time plot. At 25.0 and 0.5 °C, the first-order racemization rate constants were 0.12 ± 0.05 and $0.012 \pm 0.004\ s^{-1}$, respectively.

The relative inertness of the $Cr(phen)_3^{2+}$ toward racemization could also be demonstrated directly. An excess of Cr^{2+} ion was added to $(+)_D$-$Cr(phen)_3^{3+}$ (0.8 mM) in water at 25 °C and the rotation of the resultant $Cr(phen)_3^{2+}$ was measured at various times, using a number of wavelengths. At 25.0 °C, $k(\text{racemization}) = 0.21 \pm 0.08\ s^{-1}$. The agreement between the racemization rate constants obtained by the two approaches is fair. The reaction between $Cr(phen)_3^{3+}$ and Cr^{2+} ions could be shown to be rapid, complete within mixing times, in separate stopped-flow experiments. Interaction of Cr^{2+} with $Cr(phen)_3^{2+}$ (to form lower species) was observed to be substantially slower than racemization. The dissociation rate constant of the $Cr(phen)_3^{2+}$ has been subsequently measured, and the value confirms this observation.[8,9]

A quenched-flow technique with rapid mixers[4] was required in order to measure the racemization rate of $Co(phen)_3^{2+}$. This ion was generated by reduction of $(+)_D$-$Co(phen)_3^{3+}$ (ref 5) with $Cr(bipy)_3^{2+}$ and destroyed by $Fe(bipy)_3^{3+}$, both reduction and oxidation processes being complete within 5 ms. A standard flow rate and differing lengths of tubing between the "reduction-mixer" and "oxidizing-mixer" represent different times for racemization of the generated cobalt(II) complex. Experiments were carried out at 25 and 0.5 °C.

Table I. Rate Parameters for Ligand Dissociation and Racemization of $M(phen)_3^{2+}$ Ions at 25 °C

M	k_{diss}, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	k_{rac}, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	Ref
Cr	0.017	23.3	0.123	15	8, 9, *a*
Fe	7×10^{-5}	31.5	6.5×10^{-4}	28	*b*
Co	0.16	20.2	6.9	7.5	*a, c*
Ni	7.5×10^{-6}	24.6	9.4×10^{-6}	24.3	*d*

[a] This work. [b] F. Basolo, J. C. Hayes, and H. M. Neumann, *J. Am. Chem. Soc.*, 76, 3807 (1954). [c] P. Ellis and R. G. Wilkins, *J. Chem. Soc.*, 299 (1959). [d] R. G. Wilkins and M. J. G. Williams, *ibid.*, 1763 (1957).

We now have data for the racemization and dissociation rate constants for a number of tris(phenanthroline) complexes, $M(phen)_3^{2+}$, where M = Cr, Fe, Co, and Ni.[10,11] These are collected in Table I. For M = Cr, Fe, and Co, an intramolecular path (not involving complete cleavage of one phenanthroline ligand) is an important or even overriding component of the racemization process. Only for M = Ni is racemization an intermolecular process. It has been suggested[10,12] that $Fe(phen)_3^{2+}$ racemizes by an intramolecular mechanism because the inner sphere of the iron(II) can expand (thus permitting loss of optical activity) as a result of excitation of t_{2g} electrons to an empty e_g orbital. This mechanism could also accommodate the behavior of low spin $Cr(phen)_3^{2+}$ and "near" low spin $Co(phen)_3^{2+}$ ions, since empty e_g orbitals are also available for electron excitations. An excited state utilizing empty e_g orbitals is not possible with $Ni(phen)_3^{2+}$ since it is already in the high spin state. The purely dissociative mechanism is therefore utilized only by this ion.

Registry No. $Cr(phen)_3^{2+}$, 47836-39-5; $(+)_D$-$Cr(phen)_3^{3+}$, 60325-11-3; $Co(phen)_3^{2+}$, 16788-34-4; $(+)_D$-$Co(phen)_3^{3+}$, 24501-38-0.

References and Notes

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(6) Separate experiments on a stopped-flow apparatus showed that with the concentrations used in our experiments the reduction and oxidation reactions were complete within mixing time, a result which would be anticipated from the known redox labilities of the various couples. The time of existence of the $Cr(phen)_3^{2+}$ species was considered therefore to be that which elapsed between addition of $Cr(bipy)_3^{2+}$ and quenching by $Fe(pbipy)_3^{3+}$ but could be assessed only within 1–2 s.

(7) The $Fe(bipy)_3^{2+}$ ion in the final solution was destroyed by the addition of acid. No racemization of $Cr(phen)_3^{3+}$ occurred during the time of the experiment or by the acid treatment.

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