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Electron Exchange between Bis(η^6-arene)chromium(I) and Bis(η^6-arene)chromium(0). Comparisons between Experimental and Calculated Kinetics Parameters

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Abstract: Comparisons have been made between kinetics parameters for the self-exchange of $(\eta^6\text{-arene})_2\text{Cr}^{\text{I}}/(\eta^6\text{-arene})_2\text{Cr}^0$ (where arene = benzene, toluene, methoxybenzene, biphenyl, ethyl benzoate, and chlorobenzene) measured by ESR line broadening in dimethyl sulfoxide and the predictions from contemporary electron-transfer theory. The biphenyl system was additionally studied in a number of other solvents. These reactions provide especially tractable systems with which to test theories of outer-sphere electron transfer since the work terms should be essentially zero and the inner-shell contributions ΔG^*_{in} to the free energy barrier are small and can be estimated from infrared spectroscopy combined with crystallographic data. The solvent dependence of the rate constants for $(C_6H_5C_6H_5)_2\text{Cr}^{\text{I}/0}$ self-exchange was found to be in reasonable agreement with the predictions of the dielectric continuum model. Frequency factors were derived from the experimental rate constants coupled with the estimates of ΔG^*_{in} and values of the outer-shell contribution ΔG^*_{out} obtained by using the dielectric continuum model. These were found to be somewhat (ca. 5–20-fold) larger than the corresponding frequency factors derived from the experimental activation enthalpies combined with the dielectric continuum estimates of the activation entropies. These "experimental" frequency factors are compared with the estimates obtained from the "reactive collision" and the "ion-pair preequilibrium" models. The majority of the experimental frequency factors were found to be numerically closer to the predictions of the former model. However, the experimental values were found to decrease substantially with the addition of substituents on the arene ring, indicating the importance of steric effects. It is suggested that the discrepancies between the experimental results and the predictions of the preequilibrium model observed for these and other systems may be due to a combination of steric and nonadiabatic effects.

Outer-sphere electron-exchange reactions constitute an especially interesting class of chemical reactions in solution in that it is anticipated that quantitative theoretical descriptions of the reaction dynamics can be provided in many cases. Theoretical treatments of varying levels of complexity (and usefulness) have been developed that allow detailed insight into the physical processes involved.[1] Some recent treatments outline a useful framework within which various aspects of the theories may be tested by comparison with experimental data.[2-4]

One question that has arisen is the choice of the frequency factor for outer-sphere reactions.[2,3] Two alternative models have been proposed.[2] The "reactive collision" model considers that electron transfer occurs upon collision between appropriately energetic reactants, leading to the formulation

$$k = \kappa\Gamma_n Z[\exp(-w/RT)\exp(-\Delta G^*/RT)] \qquad (1)$$

where k is the observed (second order) rate constant for electron exchange, κ is the electronic transmission coefficient, Γ_n is a nuclear tunneling factor, Z is the collision frequency, w is the work required to form the collision complex from the separated reactants, and ΔG^* is the free energy of activation for the *elementary* electron-transfer step.[2,3] The alternative "preequilibrium" model considers that reaction occurs by activation within a previously formed bimolecular assembly.[2,3] This leads to the expression

$$k = \kappa\Gamma_n K_p{}^\circ \nu_p[\exp(-w/RT)\exp(-\Delta G^*/RT)] \qquad (2)$$

where $K_p{}^\circ$ is the equilibrium constant for formation of the "precursor complex" in the absence of work terms (i.e., when $w = 0$), ν_p is the frequency factor for activation within the precursor complex, and the other terms have the same significance as in eq 1. These two formulations therefore differ in the overall preexponential factor in that the "classical" frequency factor A equals the collision frequency Z in eq 1 but is replaced by the composite term $K_p{}^\circ\nu_p$ in eq 2. Although the collision formulation is most commonly employed for bimolecular solution reactions, including electron-transfer processes, the preequilibrium model may provide a more appropriate description of outer-sphere electron transfer when the reaction is expected to take place via electron tunneling between weakly interacting species.

Comparisons between the predictions of eq 1 and 2 with experimental data can be made by obtaining estimates of the frequency factor A in two ways. First, the observed rate constant at a given temperature can be combined with theoretical values of ΔG^*, w, κ, and Γ_n to yield estimates of A (method a). Second, the Arrhenius activation energy, E_a, derived from the observed temperature dependence of k, can be corrected for the temperature dependences of κ, Γ_n, and A to yield an "experimental value" of the enthalpic component of ΔG^*, ΔH^*. Values of A can then be found by combining this value of ΔH^* and a value of k at a given temperature with theoretical estimates of ΔS^*, w, κ, and Γ_n (method b). Since both methods depend critically upon the assumed values of ΔG^* or ΔS^*, w, κ, and Γ_n, it is clearly important to select systems for which these parameters can be estimated with confidence. Suitable redox couples will therefore be those for which the structural differences between the oxidized and the reduced form are known, and preferably small, so that the inner-shell contribution to ΔG^* can be calculated and Γ_n will be close to unity.[4] Additionally, it is desirable that the reactants be spherical, or nearly so, and the product of the reactant charges be small so that the work term, w, is small and the outer-shell (solvent) contribution to ΔG^* is most likely to conform to the prediction of the conventional dielectric continuum model.

Several tests of eq 1 and 2 have recently been made. Brown and Sutin[2] studied the self-exchange of Ru(III)/Ru(II) couples containing polypyridine and/or ammine ligands in aqueous solution. Better agreement between the experimental rate constants and activation parameters was obtained by using the reactive collision rather than the preequilibrium formulation. Similar findings were reported by Meyer et al. in a study of electron

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Table I. Calculated Reorganization Energies and Related Parameters for the Self-Exchange of Bis(η^6-arene)chromium(I)/(0) in Me_2SO at 22 °C

	arene					
	C_6H_6	$C_6H_5CH_3$	$C_6H_5OCH_3$	$(C_6H_5)_2$	$C_6H_5COOC_2H_5$	C_6H_5Cl
r, Å[a]	7.3	8.4	7.8	11.6	9.6	8.6
Δa, Å	0.07	0.06	0.08	0.07	0.04	0.04
$\nu_1{}^a$, $\nu_0{}^a$, cm^{-1}	490, 466	489, 470	490, 464	489, 465	480, 468	481, 468
$\Delta G_{in}(T)$, kcal·mol^{-1} [b]	1.15	0.85	1.55	1.30	0.45	0.50
$\Delta G^*{}_{out}$, kcal·mol^{-1} [c]	4.9	4.3	4.6	3.1	3.8	4.2
$\Delta G^*{}_{calcd}$, kcal·mol^{-1} [d]	6.1	5.2	6.2	4.4	4.3	4.7
$\Delta S^*{}_{calcd}$, cal·deg^{-1}·mol^{-1} [e]	−1.0	−0.9	−1.2	−0.9	−0.8	−0.8

[a] The average "side-by-side" internuclear distance (Cr^0–Cr^+) as estimated from molecular models. [b] Calculated using eq 3. [c] Calculated using eq 4. Sources for dielectric constants: D_{op}, ref 22; D_s, ref 21. [d] The sum of $\Delta G^*{}_{in}(T)$ and $\Delta G^*{}_{out}$. [e] The sum of $\Delta S^*{}_{in}(T)$ and $\Delta S^*{}_{out}$. $\Delta S^*{}_{in}(T)$ is taken from the temperature derivative of $\Delta G^*{}_{in}(T)$: $\Delta S^*{}_{in}(T) = -[d\Delta G^*{}_{in}(T)/dT] = -[\Delta G^*{}_{in}(T)/T][1 - (h\nu_{in}/2kT)\ \mathrm{csch}\ (h\nu_{in}/2kT)]$, where ν_{in} is the average frequency of inner-shell motion (symmetric stretch), from $\nu_{in} = [2\nu_0{}^2\nu_1{}^2/(\nu_0{}^2 + \nu_1{}^2)]^{1/2}$. $\Delta S^*{}_{out}$ is calculated from eq 6 using values of dD_{op}/dT and dD_s/dT obtained from sources given in footnote *c*.

exchange of $[Ru_3O(CH_3CO_2)_6(py)_3]^{+/0}$ in dichloromethane.[5] Systems of this latter type, where one form of the redox couple is uncharged, have the important advantage that the electrostatic work required to form the encounter complex should be essentially zero.

We have recently reported rate constants and activation parameters for the self-exchange of various $(\eta^6\text{-arene})_2Cr^{+/0}$ couples, $Cr(C_6H_5X)_2{}^{+/0}$, where X = H, CH_3, OCH_3, C_6H_5, $COOC_2H_5$, or Cl, in dimethyl sulfoxide (Me_2SO), by using the ESR line-broadening technique.[6] The self-exchange of $Cr(C_6H_5C_6H_5)_2{}^{+/0}$ was additionally studied in six other solvents. These reactants provide especially suitable systems with which to test models of outer-sphere electron transfer. Besides the likely absence of electrostatic work terms, they have the advantage that the inner-shell components $\Delta G^*{}_{in}$ are small and can be calculated from appropriate structural data. The comparison of rate constants and activation parameters for such a series of redox couples with various ring substituents can therefore provide a means of exploring the influence of reactant asymmetry on the frequency factors for electron exchange. Such comparisons between the experimental rate parameters and the predictions of eq 1 and 2 are given in the present report.

Experimental Section

The syntheses of all bis(η^6-arene)chromium compounds were described in ref 6. Infrared spectra were obtained by means of a Perkin-Elmer 457 spectrometer by using either KBr pellets or Nujol mulls at room temperature. The reported IR frequencies are accurate to ±0.5 cm^{-1}. The Nujol mulls of the air-sensitive Cr(0) complexes were prepared in an argon-filled drybox, and the spectra were measured in an argon atmosphere.

Results and Discussion

Reorganization Energies. The contribution to ΔG^* arising from inner-shell reorganization, $\Delta G^*{}_{in}(T)$, for each self-exchange reaction was calculated by means of the expression[7]

$$\Delta G^*{}_{in}(T) = \frac{2nf_0f_1(\Delta a)^2k_BT}{f_0y_1 + f_1y_0} \tag{3}$$

In eq 3, f_0 and f_1 are the force constants for the metal–arene bonds in the Cr^0 and Cr^I oxidation states, Δa is the difference in the corresponding equilibrium bond distances, n is the number of metal–ligand bonds involved, and $y_i = h\nu_i \coth (h\nu_i/4k_BT)$, where ν_i are the observed Cr–arene stretching frequencies for the oxidation state i. [Equation 3 takes into account the nuclear tunneling factor Γ_n at a given temperature; thus $\Delta G^*{}_{in}(T)$ is related to the classical inner-shell reorganization energy $\Delta G^*{}_{in}$ by $\Delta G^*{}_{in}(T) = \Delta G^*{}_{in} - RT \ln \Gamma_n$.[4] However, Γ_n is close to unity (1.0–1.2) for the present systems.] The normal vibrations of $Cr(C_6H_6)_2$ and $Cr(C_6H_6)_2{}^+$ have been assigned to be of D_{6h} symmetry from the infrared spectra,[8] so n can be set equal to 2. The force constants f_0 and f_1 in eq 3 refer to the symmetrical stretching vibration of the two arene rings with respect to the chromium atom. The frequencies of these symmetrical vibrations, ν_0 and ν_1, have been determined for the $Cr(C_6H_6)_2{}^{+/0}$ couple to be about 270 cm^{-1} and 279 cm^{-1}, respectively,[8c] allowing the force constants to be determined from $f = 5.89 \times 10^{-2}\nu m_Y$, where m_Y is the mass of one arene ring. Value of ν_0 and ν_1 for the other arenes studied here are unavailable. However, they are unlikely to be greatly different from those for $Cr(C_6H_6)_2{}^{+/0}$; thus the asymmetrical Y–Cr–Y stretching frequencies $\nu_0{}^a$ and $\nu_1{}^a$ are within 5–10 cm^{-1} for all the Cr(I) and Cr(0) arenes (Table I). The values of f_0 and f_1 were therefore estimated by assuming that $\nu_0 = 270$ cm^{-1} and $\nu_1 = 279$ cm^{-1}.

The value of Δa is 0.07 Å for the $Cr(C_6H_6)_2{}^{+/0}$ couple as found from X-ray crystallographic data.[9] For the other Cr(I)/Cr(0) couples, estimates were obtained from the corresponding difference in infrared stretching frequencies by assuming that $\Delta a \propto f_0{}^a - f_1{}^a$, where $f_0{}^a$ and $f_1{}^a$ are the force constants for the asymmetric vibrations obtained from $\nu_0{}^a$ and $\nu_1{}^a$ by using the formula $f^a = 5.89 \times 10^{-2}(\nu^a)^2[m_{Cr}m_Y/(m_{Cr} + 2m_Y)]$, where m_{Cr} is the mass of the chromium atom.[8a,c] The required proportionality constant was determined from the experimental data for $Cr(C_6H_6)_2{}^{+/0}$. Justification for this procedure is available for metallocenes.[10] The estimates of $\Delta G^*{}_{in}(T)$ resulting from inserting the appropriate values of f_0, f_1, and Δa into eq 3 are given in Table I. It is seen that the values of $\Delta G^*{}_{in}(T)$ are mostly below 1–1.5 kcal·mol^{-1}, indicating that inner-shell reorganization provides only a small contribution to the electron-transfer barrier. This is expected since the orbital into which the electron is transferred, a_{1g} having d_{z^2} symmetry, is essentially nonbonding[11] so that it may contain one or two electrons [as in Cr(I) and Cr(0), respectively] with little change in the metal–arene bonding.

The other contribution to ΔG^* is provided by the "outer-shell" reorganization energy of the surrounding solvent, $\Delta G^*{}_{out}$. This component was calculated by using the dielectric continuum expression[12]

$$\Delta G^*{}_{out} = \frac{e^2}{4}\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \tag{4}$$

where D_{op} and D_s are the optical and static dielectric constants, respectively, a_1 and a_2 are the radii of the two (spherical) reactants, r is the distance between the two reacting centers in the activated state, and e is the electronic charge. For the reactions considered

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Table II. Comparison of Experimental and Calculated Enthalpies of Activation for the Self-Exchange of Bis(η^6-arene)chromium(I)/(0) in Me_2SO at 22 °C

		exptl		calcd
arene	$10^{-7}k$, $M^{-1}\cdot s^{-1}$ [a]	ΔH^*_{pe}, kcal·mol^{-1} [b]	ΔH^*_{rc}, kcal·mol^{-1} [c]	ΔH^*_{calcd}, kcal·mol^{-1} [d]
C_6H_6	6.0	4.0	3.7	5.7
$C_6H_5CH_3$	3.3	4.6	4.3	5.0
$C_6H_5OCH_3$	7.7	3.6	3.3	5.8
$(C_6H_5)_2$	23	2.6	2.3	4.2
$C_6H_5COOC_2H_5$	32	2.3	2.0	4.1
C_6H_5Cl	20	2.9	2.6	4.4

[a] Experimental rate constant, taken from ref 6. [b] Obtained from $\Delta H^*_{pe} = E_a$, where E_a is the Arrhenius activation energy. [c] Obtained from $\Delta H^*_{rc} = E_a - 0.5\,RT$. [d] Calculated enthalpies of activation, obtained from $\Delta H^*_{calcd} = \Delta G^*_{calcd} + T\Delta S^*_{calcd}$ using values of ΔG^*_{calcd} and ΔS^*_{calcd} given in Table I.

here, it is reasonable to assume that approximately $r = 2a_1 = 2a_2$ so that eq 4 reduces to

$$\Delta G^*_{out} = \frac{e^2}{4r}\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \tag{5}$$

The values of r for each reaction were calculated by assuming that the transition state is formed with the two reactants placed "side by side" (i.e., with the arene rings lying in the same plane)[6] and by using the reported bond distances and van der Waals radii.[9,13] These estimates of r and the resulting values of ΔG^*_{out} obtained from eq 4 by using known values of D_{op} and D_s are given in Table I (see footnotes for data sources). Also listed in Table I are the calculated values of ΔG^*, ΔG^*_{calcd}, obtained for each reaction from the sum of the corresponding values of ΔG^*_{in} and ΔG^*_{out}.

In addition to the free energies of reorganization, it is also necessary to calculate values of the enthalpic and entropic components of ΔG^*, ΔH^* and ΔS^*, respectively. The outer-shell component of ΔS^*, ΔS^*_{out}, was determined from the temperature derivative of ΔG^*_{out}:

$$\Delta S^*_{out} = -\left(\frac{d\Delta G^*_{out}}{dT}\right) = \frac{e^2}{4r}\left(\frac{1}{D_{op}^2}\frac{dD_{op}}{dT} - \frac{1}{D_s^2}\frac{dD_s}{dT}\right) \tag{6}$$

The inner-shell component of ΔS^*, ΔS^*_{in}, was calculated from the temperature derivative of $\Delta G^*_{in}(T)$ (eq 3), thereby taking into account the (small) temperature dependence of Γ_n.[4] The resulting values of ΔS^*_{in} (−0.3 to −0.6 eu) were then summed with the corresponding estimates of ΔS^*_{out} to yield the calculated activation entropies ΔS^*_{calcd} listed in Table I.

Comparison of Experimental and Theoretical Kinetics Parameters. As noted in the introduction, tests of the applicability of eq 1 or 2 to describe the experimental kinetics parameters can be made either by combining the experimental rate constant at a given temperature with a theoretical estimate of ΔG^* (method a) or by employing both the rate constant and its temperature derivative along with a theoretical estimate of ΔS^* (method b). The resulting "experimental" frequency factors can be compared with the values of Z and $K_p^\circ \nu_p$ calculated by using various models. Alternatively, the calculated frequency factors can be combined with the observed rate constant and activation parameters to yield "experimental" values of ΔG^* and ΔS^*, which can be compared with the corresponding theoretical estimates. Clearly, the reliability with which a given model for calculating frequency factors can be tested depends sensitively on the accuracy with which ΔG^* or ΔS^* can be calculated, and vice versa. However, the experimental enthalpies of activation ΔH^* obtained from the temperature dependence of the rate constants are insensitive to the particular model employed for the frequency factor. Therefore the comparison between the experimental and calculated values of ΔH^* provides a useful independent test of the likely validity of such theoretical reorganization parameters.

Table III. Comparison of Calculated and "Experimental" Frequency Factors ($M^{-1}\cdot s^{-1}$) for the Self-Exchange of Bis(η^6-arene)chromium(I)/(0) in Me_2SO at 22 °C

	calcd freq factors		"exptl" freq factors	
arene	A^{pe}_{calcd} (eq 8)	A^{rc}_{calcd} (eq 9)	A_a (eq 7a)	A_b (eq 7b)
C_6H_6	3.5×10^{12}	2.5×10^{11}	1.7×10^{12}	9.1×10^{10}
$C_6H_5CH_3$	5.3×10^{12}	3.1×10^{11}	2.4×10^{11}	1.3×10^{11}
$C_6H_5OCH_3$	5.9×10^{12}	2.5×10^{11}	2.8×10^{12}	6.5×10^{10}
$(C_6H_5)_2$	1.7×10^{13}	4.7×10^{11}	4.5×10^{11}	3.1×10^{10}
$C_6H_5COOC_2H_5$	9.1×10^{12}	3.3×10^{11}	4.9×10^{11}	2.4×10^{10}
C_6H_5Cl	6.2×10^{12}	3.0×10^{11}	6.1×10^{11}	4.2×10^{10}

Table II contains a comparison of experimental and calculated values of ΔH^* for the various Cr(I)/Cr(0) self-exchange reactions in Me_2SO. Two "experimental" values of ΔH^* are listed for each reaction. The first type, labeled ΔH^*_{pe}, is equal to the Arrhenius activation energy, $E_a = R[\partial \ln k/\partial(1/T)]$; these values are consistent with the preequilibrium formulation since the preexponential factor in this model ($\kappa\Gamma_n K_p^\circ \nu_p$, eq 2) is expected to be essentially independent of temperature. The second type, labeled ΔH^*_{rc}, is uniformly 0.3 kcal·mol^{-1} ($=RT/2$) smaller than ΔH^*_{pe}; these correspond to the use of the reactive collision formulation since the collision frequency Z appearing in eq 1 is expected to be proportional[2] to $T^{1/2}$. The calculated values of ΔH^*, labeled ΔH^*_{calcd} in Table II, were obtained from the corresponding values of ΔG^*_{calcd} and ΔS^*_{calcd} given in Table I by using $\Delta H^*_{calcd} = \Delta G^*_{calcd} + T\Delta S^*_{calcd}$.

It is seen that both ΔH^*_{pe} and ΔH^*_{rc} are uniformly smaller than the corresponding values of ΔH^*_{calcd} by amounts varying from ca. 0.5 to 2 kcal·mol^{-1}. Since the estimates of ΔH^*_{in} are likely to be correct within at least ca. 0.5 kcal·mol^{-1}, it seems likely that these discrepancies are due chiefly to theoretical estimates of the outer-shell component ΔH^*_{out} that are somewhat too large.

Nonetheless, if we assume for the moment that the theoretical reorganization parameters ΔG^*_{calcd} or ΔS^*_{calcd} given in Table I are correct, these quantities can be combined with the experimental rate constants k given in Table II[14] to yield "experimental" estimates of the frequency factors A_a and A_b by using the relation

$$k = A_a \exp(-\Delta G^*_{calcd}/RT) \tag{7a}$$

or

$$k = A_b \exp(-\Delta H^*/RT) \exp(\Delta S^*_{calcd}/R) \tag{7b}$$

where ΔH^* in eq 7b is obtained from the experimental Arrhenius slope (most simply by assuming that A_b is independent of temperature; i.e., $\Delta H^* = \Delta H^*_{pe}$). The resulting values of A_a and A_b are listed in Table III, along with the frequency factors A^{pe}_{calcd} and A^{rc}_{calcd} calculated from the conventional forms of the preequilibrium and reactive collision models given by eq 8 and 9, respectively:[2,3]

$$A^{pe}_{calcd} = \nu_p K_p^\circ \exp(-w/RT) = \left(\frac{\nu_{in}^2 \Delta G^*_{in}}{\Delta G^*_{calcd}}\right)^{1/2} \frac{4\pi N r^3}{3000} \exp(-w/RT) \tag{8}$$

$$A^{rc}_{calcd} = Z \exp(-w/RT) = (N/10^3)[8\pi k_B T(m_1 + m_2)/m_1 m_2]^{1/2} r^2 \exp(-w/RT) \tag{9}$$

where N is Avogadro's number, m_1 and m_2 are the masses of the

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[14] The rate constants k reported in ref 6 which were used in Table II and elsewhere in the present paper were obtained in the absence of a background electrolyte (reactant concentrations 10^{-4}–10^{-3} M). The addition of $KClO_4$ had only a negligible influence upon k (<10%) even up to 0.5 M, although small yet significant decreases in k (≲20%) were observed upon the additon of KPF_6. This latter influence may be due to slight ion association. These results support the contention that the work terms w, at least those arising from simple electrostatic interactions, are negligible for these systems.

Table IV. Comparison of "Experimental" and Calculated Free Energies and Entropies of Activation for the Self-Exchange of Bis(η^6-arene)chromium(I)/(0) in Me_2SO at 22 °C

arene	act. free energies, kcal·mol^{-1}			act. entropies, cal·deg^{-1}·mol^{-1}		
	ΔG^*_{pe}[a]	ΔG^*_{rc}[b]	ΔG^*_{calcd}[c]	ΔS^*_{pe}[d]	ΔS^*_{rc}[e]	ΔS^*_{calcd}[f]
C_6H_6	6.4	5.0	6.1	−8.1	−4.4	−1.0
$C_6H_5CH_3$	7.0	5.2	5.2	−8.1	−3.1	−0.9
$C_6H_5OCH_3$	6.6	4.7	6.2	−10.1	−4.9	−1.2
$(C_6H_5)_2$	6.5	4.4	4.4	−13.2	−7.1	−0.9
$C_6H_5COOC_2H_5$	6.0	4.0	4.3	−12.1	−7.0	−0.8
C_6H_5Cl	6.1	4.3	4.7	−10.6	−5.7	−0.8

[a] Obtained from $\Delta G^*_{pe} = -RT \ln (k/A^{pe}_{calcd})$. [b] Obtained from $\Delta G^*_{rc} = -RT \ln (k/A^{rc}_{calcd})$. [c] Sum of ΔG^*_{out} and $\Delta G^*_{in}(T)$; taken from Table I. [d] Obtained from $\Delta S^*_{pe} = (\Delta G^*_{pe} - \Delta H^*_{pe})/T$; ΔH^*_{pe} taken from Table II. [e] Obtained from $\Delta S^*_{rc} = (\Delta G^*_{rc} - \Delta H^*_{rc})/T$; ΔH^*_{rc} taken from Table II. [f] Sum of ΔS^*_{out} and $\Delta S^*_{in}(T)$; taken from Table I.

two reactants, w is the electrostatic work required to form the collision complex from the separated reactants, and ν_{in} (s^{-1}) is the effective frequency of the inner-shell motion (metal–ligand vibration); this was obtained from the symmetrical stretching frequencies ν_0 and ν_1 (270 and 279 cm^{-1}, respectively) by using[4] $\nu_{in} = c[2\nu_0^2\nu_1^2/(\nu_0^2 + \nu_1^2)]^{1/2}$, where c is the velocity of light. Since one of the reactants is uncharged, it is assumed that $w = 0$.[14]

Inspection of Table III reveals that the "experimental" frequency factors A_a are, in the majority of cases, close to (within a factor of 2) the values of A^{rc}_{calcd}, although ca. 5–20-fold smaller than A^{pe}_{calcd}. The frequency factors A_b derived from the experimental rate constants and the activation energies along with ΔS^*_{calcd} (eq 7b) are seen to be significantly smaller, ca. $^1/_{20}$ of the corresponding values of A_a (Table III). These latter discrepancies result from the differences between the experimental and calculated values of ΔH^* (Table II), since the determination of A_a utilizes ΔG^*_{calcd}, whereas the determination of A_b employs only the entropic component ΔS^*_{calcd} (eq 7a,b). On the basis of the present evidence, it is difficult to decide whether A_a or A_b more closely approximates the true frequency factors; clearly, the choice depends upon whether ΔG^*_{calcd} or ΔS^*_{calcd} is considered more reliable. It has been suggested[2] that the activation entropy ΔS^* can be taken as zero for self-exchange reactions since $\Delta S^*_{in} \approx 0$ and ΔS^*_{out} is also predicted to be approximately zero from the dielectric continuum model. If indeed $\Delta S^* \approx 0$, then the smaller frequency factors A_b will be approximately correct. However, since the experimental activation enthalpies are smaller than the calculated values, it is likely that there would be a corresponding discrepancy between the actual and calculated activation entropies via a "compensation effect",[15] so that $\Delta S^* < \Delta S^*_{calcd}$. For example, the effect could arise from an increase in specific solvent polarization required to form the transition state from the separated reactants, yielding an unexpected negative contribution to both ΔH^* and ΔS^*. Consequently, the actual frequency factors may well be larger than A_b and close to A_a. The latter corresponds to the situation in which the discrepancies between the actual and calculated enthalpic and entropic components of ΔG^* cancel, so that the actual free energies of activation approximately equal ΔG^*_{calcd}.

The comparison between the predictions of the preequilibrium and collision models and the experimental kinetic parameters can equivalently be presented in terms of reorganization energies. Table IV contains values of free energies of activation ΔG^*_{pe} and ΔG^*_{rc} obtained from the observed rate constants by using frequency factors calculated from the preequilibrium and collision models, respectively (eq 8 and 9). Listed alongside are the theoretical estimates ΔG^*_{calcd} from Table I. It is seen that the corresponding values of ΔG^*_{rc} and ΔG^*_{calcd} for most of the reactions agree closely (within 0.3 kcal·mol^{-1}), paralleling agreement between A_a and A^{rc}_{calcd}, whereas the corresponding values of ΔG^*_{pe} are significantly (1.5–2 kcal·mol^{-1}) larger. Similar results have been obtained previously for several other outer-sphere self-exchange reactions.[2-5] Table IV also contains estimates of activation entropies ΔS^*_{pe} and ΔS^*_{rc} obtained by combining the observed rate constants and activation energies along with A^{pe}_{calcd} and A^{rc}_{calcd}. It is seen that the values of ΔS^*_{rc} are uniformly 3–6 eu more negative than ΔS^*_{calcd}, which follows since $A_b < A_a$, A^{rc}_{calcd} (Table III). The values of ΔS^*_{pe} (−8 to −13 eu) seem unreasonably negative; a large increase in the extent of solvent ordering in the transition state compared to that for the separated reactants seems unlikely for the present systems. Consequently, it appears that the values of A^{rc}_{calcd} listed in Table III are too large.

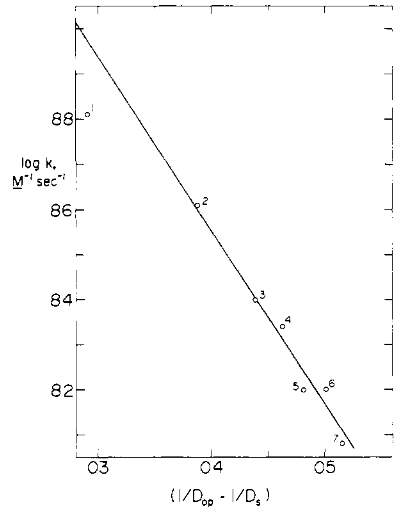

Figure 1. Plot of logarithm of rate constant k for self-exchange of $Cr(C_6H_5C_6H_5)_2^{+/0}$ in various solvents vs. $1/D_{op} - 1/D_s$, where D_{op} and D_s are the optical and static dielectric constants for each solvent: 1, 9/1 (v/v) C_6H_6/CH_3OH; 2, benzonitrile; 3, dimethyl sulfoxide; 4, dimethylformamide; 5, 1/4 (v/v) C_6H_6/CH_3OH; 6, propylene carbonate; 7, 1/7 (v/v) C_6H_6/CH_3OH. Values of k given in Table V; sources for D_{op} and D_s given in footnote h to Table V.

Another method of estimating the frequency factor involves monitoring the rate constant for a given exchange reaction in several solvents. Since we can write

$$k = A \exp[-(\Delta G^*_{in} + \Delta G^*_{out})/RT] \quad (10)$$

if ΔG^*_{out} is given by the dielectric continuum model (eq 5), then

$$\log k = \log A - \Delta G^*_{in}/2.303RT - \frac{e^2}{2.303 \times 4rRT}\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \quad (11)$$

Therefore, a plot of log k vs. $1/D_{op} - 1/D_s$ should allow A to be obtained from the intercept, and r from the slope. Such a plot is shown for the $Cr(C_6H_5C_6H_5)_2^{+/0}$ self-exchange reaction in seven solvents in Figure 1. The rate data are taken from ref 6 and were corrected for the effects of diffusion in the conventional manner by using $k^{-1} = k_{app}^{-1} - k_{diff}^{-1}$, where k_{app} is the measured (apparent) rate constant and $k_{diff} = 8RT/3000\eta$, where η is the solvent viscosity. (This correction turned out to be small, yet significant in several solvents.) The values of k are also listed in Table V.

It is seen that the variation of k among most of the solvents studied is approximately in accord with eq 1, suggesting that the

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[15] See, for example: Lumry, R.; Rajender, S. *Biopolymers* **1970**, *9*, 1125.

Table V. Rate Constants, Activation Parameters, and Experimental Frequency Factors A ($M^{-1}\cdot s^{-1}$) for the Self-Exchange of $(C_6H_5C_6H_5)_2Cr^{I/0}$ in Various Solvents at 22 °C

	$10^{-8}k$,[a]	act. enthalpies, $kcal\cdot mol^{-1}$			act. entropies, $cal\cdot deg^{-1}\cdot mol^{-1}$			"exptl" freq factors, $M^{-1}\cdot s^{-1}$	
solvent	$M^{-1}\cdot s^{-1}$	ΔH^*_{pe}[b]	ΔH^*_{rc}[c]	ΔH^*_{calcd}[d]	ΔS^*_{pe}[e]	ΔS^*_{rc}[f]	ΔS^*_{calcd}[g]	A_a (eq 7a)[h]	A_b (eq 7b)[h]
9/1 (v/v) C_6H_6/CH_3OH	6.4	2.3	2.0		−12.6	−6.4		2.1×10^{11}	
benzonitrile	4.1	2.7	2.4	3.8	−11.9	−6.1	−1.4	4.2×10^{11}	7.7×10^{10}
dimethyl sulfoxide	2.5	2.6	2.3	4.2	−13.2	−7.4	−0.9	4.5×10^{11}	3.1×10^{10}
dimethylformamide	2.2	3.1	2.8	4.1	−11.5	−5.8	−1.9	5.5×10^{11}	1.0×10^{11}
1/4 (v/v) C_6H_6/CH_3OH	1.6	3.7	3.4		−10.2	−4.4		6.8×10^{11}	
propylene carbonate	1.6	3.9	3.6	4.5	−9.5	−3.7	−0.8	5.0×10^{11}	1.7×10^{11}
1/7 (v/v) C_6H_6/CH_3OH	1.2	3.8	3.5		−10.2	−4.7		5.8×10^{11}	

[a] Experimental rate constant corrected for diffusion (see text), using viscosity data given in ref 21. [b] Obtained from experimental activation energy E_a assuming that $\Delta H^*_{pe} = E_a$. [c] Obtained from E_a assuming that $\Delta H^*_{rc} = E_a - 0.5RT$. [d] Obtained as in Table II, using dielectric constants from sources given in footnote *h*. [e] Obtained from experimental rate constant and A^{pe}_{calcd} (eq (8)) as described in footnotes to Table IV. [f] Obtained from experimental rate constant and A^{rc}_{calcd} (eq 9) as described in footnotes to Table IV. [g] Obtained as in Table IV, using dielectric constants from sources given in footnote *h*. [h] Dielectric constant data required for calculating ΔG^*_{calcd} (eq 7a) and ΔS^*_{calcd} (eq 7b) obtained from following: D_{op} and D_s for benzene/methanol mixtures obtained by linear interpolation of values for pure solvents. Values of D_{op} for each solvent obtained from ref 22, except for propylene carbonate, given in: Simeral, L.; Amey, R. L. *J. Phys. Chem.* 1970, *74*, 1443. Sources for D_s: Benzene, methanol, dimethyl sulfoxide: ref 21. Benzonitrile: Maryott, A. A.; Smith, E. R. *Natl. Bur. Stand. (U.S.) Circ.* 1951, *No. 514*. Dimethylformamide: Bass, S. J.; Nathan, W. I.; Meighan, R. M.; Cole, R. H. *J. Phys. Chem.* 1964, *68*, 590. Propylene carbonate: Payne, R.; Theodorou, I. E. *Ibid.* 1972, *76*, 2892.

dielectric continuum model provides a reasonable description of the solvent influence upon ΔG^*. The straight line drawn through the points has a slope of 3.9 and a y intercept of 10.1. The resulting value of r, 15.5 Å, is roughly comparable to the value, 11.6 Å (Table I), deduced from the reactant structure by assuming a side-by-side configuration in the transition state. If we assume that $\Delta G^*_{in} = 1.3$ kcal·mol^{-1} (Table I), a frequency factor A of ca. 9×10^{10} $M^{-1}\cdot s^{-1}$ is obtained. Considering the lengthy extrapolation of Figure 1 necessary to determine A, the value is in reasonable agreement with A_a, A_b, and also A^{rc}_{calcd} but again is markedly smaller than A^{pe}_{calcd} (Table III).

Table V also contains values of A_a and A_b, determined for the self-exchange of $(C_6H_5C_6H_5)_2Cr^{I/0}$ in each solvent, which were obtained from the experimental data as in Table III. As expected, the values of A_a are largely independent of the solvent, although the values of A_b do vary somewhat and are $^1/_3$ to $^1/_{15}$ of those of A_a. This variation of A_b with the solvent most likely arises from a solvent dependence of the outer-shell entropy term ΔS^*_{out} which is larger than calculated by using the dielectric continuum model. However, it is seen from the values of ΔH^*_{pe} and ΔH^*_{rc}, also listed in Table V, that the major part of the solvent dependence of k arises from variations in the enthalpic component, as predicted from theory.

Since the collision model yields frequency factors that are in closer agreement with the experimental results than are the frequency factors obtained from the simple preequilibrium model, it might be inferred that the former model provides a more accurate description of the physical events leading to electron transfer, i.e., that outer-sphere electron transfer is consummated by collision between suitably activated reactants rather than by vibronic excitation within a preformed bimolecular assembly. However, such a conclusion may be unwarranted. Both A^{pe}_{calcd} and A^{rc}_{calcd} were calculated by assuming that the reactions are adiabatic, i.e., that $\kappa = 1$. Some recent calculations[4,16] indicate that substantially nonadiabatic pathways ($\kappa \sim 10^{-3}$–10^{-2}) may predominate even for $Fe(OH_2)_6^{3+/2+}$. Values of κ below unity for the present system would tend to bring A^{rc}_{calcd} into closer agreement with A_a and A_b. A related point is that a steric factor arising from the nonspherical shape of the reactants should probably be included in the overall frequency factor. This contention is supported by the observation that both A_a and A_b fall significantly as substituents are added to the arene rings, to an extent that is greater for larger substituents (Table III). Thus the values of both A_a and A_b for $Cr(C_6H_5C_6H_5)_2^{+/0}$ self-exchange are about 4-fold less than those for $Cr(C_6H_6)_2^{+/0}$, even though the values of A^{pe}_{calcd} and A^{rc}_{calcd} are slightly greater for the latter reaction. Even the parent arene reactants $Cr(C_6H_6)_2^{+/0}$ are not spherical; reaction may occur preferentially, for example, with the arene rings in a "side-by-side" rather than "vertically stacked" configuration.[6,17] Such steric selectivity would yield smaller values of A^{pe}_{calcd} and A^{rc}_{calcd} than obtained by using the conventional formulas (eq 8 and 9) which refer to spherical structureless reactants.

Further, the expression previously used[2-5] for the precursor "stability constant" $K_p = (4\pi Nr^3/3000)\exp(-w/RT)$, appearing in eq 8, may yield incorrectly large estimates of K_p and hence A^{pe}_{calcd}. This expression refers to the formation of contact pairs between two spherical species. It seems more appropriate to visualize K_p as being the probability of one reactant being within a given inclusion volume surrounding the other reactant within which electron transfer can occur. Most simply, the magnitude of this volume can be determined by

$$K_p = [4\pi N(d_2^3 - d_1^3)/3000]\exp(-w/RT) \qquad (12)$$

where d_1 is the minimum (contact) distance between the reactants and d_2 is the maximum distance on which electron tunneling can effectively occur. If, for example, $d_2 - d_1 = 1$ Å, eq 1 leads to values of K_p and hence A^{pe}_{calcd} for the present systems that are factors of 2–3 smaller than those obtained with eq 8. However, in reality K_p will continuously decrease as the internuclear distance increases rather than exhibit the discontinuity that is presumed in eq 12.[19] Substantially smaller ($\gtrsim$10-fold) values of K_p can also be deduced by using this model by taking into account the nonsphericity of the reactants and assuming that only certain precursor structures, such as a "side-by-side" configuration, result in electron transfer.

Consequently, the values of A^{pe}_{calcd} obtained by taking such steric and tunneling factors into account could become comparable to the experimental estimates of A_a and A_b. Also, the apparently good agreement seen between A^{pe}_{calcd} and A_a and A_b is probably misleading since the inclusion of reasonable steric factors for the present reactants into the collisional model (eq 9) would almost certainly yield values of A^{pe}_{calcd} which are markedly too small.

Conclusions

By and large, the experimental kinetics parameters are in reasonable agreement with the predictions from conventional electron-transfer theory, at least if the collision model is used to provide estimates of the effective frequency factors. However,

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it is interesting to note that the deviations observed between experiment and theory are qualitatively similar to those seen previously for other self-exchange reactions. Thus it has been found that $\Delta H^* < \Delta H^*_{\text{calcd}}$ and $\Delta S^* < \Delta S^*_{\text{calcd}}$ for ferrocinium/ferrocene in a number of solvents.[20] and for $Ru(NH_3)_4bpy^{3+/2+}$ in aqueous media.[2] Most likely, these discrepancies reflect a limitation of the dielectric continuum model, possibly arising from changes in short-range reactant–solvent interactions required to form the encounter complex "solvent cage" prior to electron transfer. The requirement of forming a particular encounter geometry, with the two reactants essentially in contact so as to maximize the transmission coefficient, may partly be responsible for the experimental frequency factors being markedly smaller than those calculated that a simple model involving activation of a precursor complex formed in a prior equilibrium step. However, the simple collision model appears to have greater practical utility for outer-sphere processes, at least for the purpose of making numerical calculations.

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Registry No. $(\eta^6\text{-}C_6H_6)_2Cr^1$, 11077-47-7; $(\eta^6\text{-}C_6H_6)_2Cr^0$, 1271-54-1; $(\eta^6\text{-}C_6H_5CH_3)_2Cr^1$, 33505-50-9; $(\eta^6\text{-}C_6H_5CH_3)_2Cr^0$, 12087-58-0; $(\eta^6\text{-}C_6H_5OCH_3)_2Cr^1$, 75170-79-5; $(\eta^6\text{-}C_6H_5OCH_3)_2Cr^0$, 57820-92-5; $(\eta^6\text{-}C_6H_5C_6H_5)_2Cr^1$, 33154-48-2; $(\eta^6\text{-}C_6H_5C_6H_5)_2Cr^0$, 33085-81-3; $(\eta^6\text{-}C_6H_5COOC_2H_5)_2Cr^1$, 57219-88-2; $(\eta^6\text{-}C_6H_5COOC_2H_5)_2Cr^0$, 57219-87-1; $(\eta^6\text{-}C_6H_5Cl)_2Cr^1$, 75170-75-1; $(\eta^6\text{-}C_6H_5Cl)_2Cr^0$, 42087-89-8.

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Coordination Modes of Histidine. 3.[1] Stereochemistry of Copper(II) Complexes Related to Pyridoxal Catalysis

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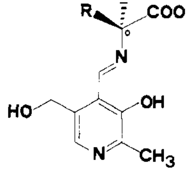
Abstract: Copper(II) complexes of Schiff bases derived from pyridoxal, salicylaldehyde, or pyruvic acid and histidine, histidine methyl ester, and representative amino acids with nonpolar side chains have been prepared by metal ion template synthesis. The mode of coordination to copper(II) of the histidine residues in these complexes has been investigated by circular dichroism spectroscopy. The complexes derived from amino acids with nonpolar side chains provide appropriate references for the glycine-like coordination mode, while the derivatives of histidine methyl ester are appropriate references for the histamine-like mode. The histidine residues exhibit a striking tendency to bind copper(II) through chelate ring types complementary to those of the fused carbonyl residue. Thus, in the complexes derived from pyridoxal and salicylaldehyde the histidine residues bind glycine-like, whereas in those derived from pyruvic acid the histidine residues bind histamine-like. The conformation of the coordinated Schiff base ligands has been deduced from the circular dichroism spectra of the complexes and discussed in relation to vitamin B_6 model reactions. The EPR spectra of the complexes were also investigated in different solvents to establish the donor sets and the ligand field symmetry in solution. The spectra show the pattern typical for tetragonal symmetry ($g_{\parallel} > g_{\perp}$), and the magnetic parameters were used to compute the molecular orbital coefficients that describe the bonding character in the complexes. The electronic excitation energies required in the calculations were deduced from the circular dichroism spectra.

Most of the transformations that amino acids undergo during metabolism are catalyzed by enzymes requiring pyridoxal phosphate as a cofactor.[2] The mechanisms proposed for pyridoxal catalysis, however, have mostly been derived from studies on model systems utilizing amino acid–pyridoxal and related Schiff bases and their metal complexes.[3,4] The work in this field has focused on mechanistic and spectroscopic properties of the systems, and only recently the enhancement of reactivity of a group to the amino acid α-carbon atom has been related to its correct stereochemical positioning within the molecule.[5] As first suggested by Dunathan,[6] an easy cleavage of a bond to the amino acid α-carbon atom in I can be accomplished by orienting that bond orthogonal to the plane of the extended π system in order to optimize σ–π overlap. This stereoelectronic requirement enables pyridoxal-dependent enzymes to achieve reaction specificity and enhance reaction rates by proper conformational orientation of the bond to be cleaved (or formed). Despite the importance of recognizing the stereochemical factors that control the correct positioning of the groups



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