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Evaluation of the Intrinsic Parameters of Octacyanomolybdate(IV) and -(V) and Hexacyanoferrate(II) and -(III) from a Kinetic Study of the Oxidation of Benzenediols

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Received November 3, 1977

The experimental rates of many outer-sphere electron-transfer reactions

$$\mathrm{Ox}_1 + \mathrm{Red}_2 \xrightarrow{k_{12}} \mathrm{Ox}_2 + \mathrm{Red}_1 \tag{1}$$

agree with the Marcus free-energy relationship

$$\Delta G^*_{12} = w_{12} + \lambda_{12}(1 + \Delta G^\circ{}_{12}'/\lambda_{12})^2/4 \tag{2}$$

where

$$k_{12} = Z\exp(-\Delta G^*_{12}/RT) \tag{3}$$

$$\lambda_{12} = 2(\Delta G^*_{11} - w_{11} + \Delta G^*_{22} - w_{22}) \tag{4}$$

$$\Delta G^\circ{}_{12}' = \Delta G^\circ{}_{12} + w_{21} - w_{12} \tag{5}$$

Z is the collision number in solution, taken to be 10^{11} M^{-1} s^{-1}; ΔG^*_{11} and ΔG^*_{22} are the activation free energies for self-exchange reactions and w_{11} and w_{22} are the related work terms; w_{12} and w_{21} are the corresponding work terms involved in bringing reactants and products together, respectively.[1]

A knowledge of ΔG^{**} (where $\Delta G^{**} = \Delta G^* - w$) for the self-exchange reactions is of obvious importance in tests of the Marcus theory; the work terms can be evaluated according to

$$w = \frac{z_1 z_2 e^2}{Dr^*}\exp(-\kappa r^*) \tag{6}$$

where z_1 and z_2 are the formal charges of the reactants, D is the static dielectric constant, and r^* is the distance between the centers of reactants; the exponential coefficient is the Debye–Hückel term with κ as the reciprocal Debye radius.[2]

It is well-known that the exponential coefficient overcorrects for ionic strength outside of the Debye–Hückel region and, in turn, the zero ionic strength extrapolation undercorrects.[3] Recently, Haim and Sutin proposed an "averaged" method for estimating the work terms and in this way obtained satisfactory agreement with experimental data.[4]

In previous work we have investigated the kinetics of electron-transfer reactions between benzenediols (H_2Q) and hexachloroiridate(IV),[5] tris(1,10-phenanthroline)iron(III) and its derivatives (FeL_3^{3+}),[6] and aquopentachloro-, diaquo-, tetrachloro-, and hexabromoiridate(IV).[7] The rate-determining step of these reactions can be represented as in eq 7,

$$\mathrm{Ox} + \mathrm{H_2Q} \rightarrow \mathrm{Red} + \mathrm{H_2Q^{+}}\cdot \tag{7}$$

and a model for calculating the free-energy changes involved was proposed.[5a] Different λ_{12}'s were found to hold for different oxidant complexes.[5-7] Since benzenediols are uncharged molecules, the term w_{12} can be set equal to zero, and w_{21} (which involves an interaction of charged metal complexes with a monopositive cation radical at ionic strength 1.0 M) can also be tentatively neglected.[8] Thus, to a good approximation, $\Delta G^\circ{}_{12}' = \Delta G^\circ{}_{12}$ for all the oxidants. Moreover, since $\lambda_{12} = 2(\Delta G^{**}_{11} + \Delta G^{**}_{22})$, with ΔG^{**}_{22} (referred to benzenediols) kept constant,[9] $\Delta\Delta G^{**}_{11} = {}^1/_2\Delta\lambda_{12}$. Thus, a relative "scale" of ΔG^{**}_{11} can be derived. A problem arises in the selection of a reference for ΔG^{**}_{11}. In a previous paper,[12] we have chosen the $IrCl_6^{2-/3-}$ system, whose self-exchange rate was determined at $\mu = 0.1$ M[13] ($\Delta G^*_{11} = 7.7$ kcal mol^{-1}; $w_{11} = 1.2$ ($r = 4.3$ Å) and thus $\Delta G^{**}_{11} = 6.5$).[14] Consequently, for $FeL_3^{3+/2+}$ ΔG^{**} should be 1.5 kcal mol^{-1},[6] for $Ir(H_2O)Cl_5^{-/2-}$ and $Ir(H_2O)_2Cl_4^{0/-}$, $\Delta G^{**} = 6.5$ kcal mol^{-1},[7] and for $IrBr_6^{2-/3-}$, $\Delta G^{**} = 4.0$ kcal mol^{-1}.[7] With these values a satisfactory agreement was found between calculated and experimental data.[7,12]

Table I. Kinetic Data for Benzenediol Oxidation by $Mo(CN)_8{}^{3-}$ [a]

Benzenediol	k, M^{-1} s^{-1} [b]	ΔG°, kcal mol^{-1} [c]	k_{calcd}, M^{-1} s^{-1} [d]
2-Methylbenzene-1,4-diol	7.6×10^4	6.1	3.0×10^4
Benzene-1,4-diol	1.1×10^4	7.8	4.3×10^3
2-Chlorobenzene-1,4-diol	3.7×10^3	8.2	2.7×10^3
4-Methylbenzene-1,2-diol	4.7×10^3	8.7	1.5×10^3
4-*tert*-Butylbenzene-1,2-diol	5.2×10^2	9.3	7.0×10^2
Benzene-1,2-diol	9.5×10^1	10.5	1.5×10^2

[a] At 20.0 °C, $[HClO_4] = 1.00$ M, $\mu = 1.0$ M; $[Mo(CN)_8{}^{3-}] = 5 \times 10^{-5}$ M; the concentration range for benzenediols was $(1-6) \times 10^{-4}$ M, except for 2-methylbenzene-1,4-diol ($(0.5-2) \times 10^{-4}$ M) and benzene-1,2-diol ($(5-20) \times 10^{-3}$ M). [b] The standard deviations are 4–6%. [c] Referred to the rate-determining step; calculated as described in ref 3; $E^\circ(Mo(CN)_8{}^{3-/4-}) = 0.80$ V.[9] [d] Calculated with eq 2; $\lambda_{12} = 21$ kcal mol^{-1}.

Table II. Kinetic Data for Benzenediol Oxidation by $Fe(CN)_6{}^{3-}$ [a]

Benzenediol	k, M^{-1} s^{-1} [b]	G°, kcal mol^{-1} [c]	k_{calcd}, M^{-1} s^{-1} [d]
2-Methylbenzene-1,4-diol	72	8.2	84
Benzene-1,4-diol	10	9.9	12

[a] At 20.0 °C, $[HClO_4] = 1.00$ M, $\mu = 1.0$ M; $[Fe(CN)_6{}^{3-}] = 1 \times 10^{-4}$ M; the concentration range of 2-methylbenzene-1,4-diol was $(1-5) \times 10^{-3}$ M and 0.10–0.20 M for benzene-1,4-diol. [b] The rate constants were estimated preferably in the early part of reaction; the standard deviation is 5–7%. [c] Referred to the rate-determining step; calculated as described in ref 3; $E^\circ(Fe(CN)_6{}^{3-/4-}) = 0.71$ V. [d] Calculated with eq 2; $\lambda_{12} = 30$ kcal mol^{-1}.

In order to evaluate the importance of the correct estimation of ΔG^{**} and of the work terms, we decided to investigate reaction 8 at $\mu = 0.010$ M and 25.0 °C. This reaction was

$$\mathrm{Mo(CN)_8{}^{3-} + Fe(CN)_6{}^{4-} \rightarrow Mo(CN)_8{}^{4-} + Fe(CN)_6{}^{3-}} \tag{8}$$

previously investigated at 0.50 M H_2SO_4,[15] whereas in the present study a lower ionic strength was chosen. Moreover, with $w_{21} = w_{12}$, then $\Delta G^\circ{}_{12}' = \Delta G^\circ{}_{12}$. In order to estimate ΔG^{**} for the two reactants, their reactions with benzenediols were also investigated.

Experimental Section

Reagents. Octacyanomolybdate(IV) was prepared according to the described procedure[16] and the corresponding Mo(V) derivative was obtained by electrooxidation. All the other chemicals were of high quality and were used without further purification. Doubly distilled water was used.

Procedure. The oxidation of benzenediols was followed at 390 nm for $Mo(CN)_8{}^{3-}$ (ϵ 1.3×10^3 M^{-1} cm^{-1}) and at 420 nm for $Fe(CN)_6{}^{3-}$ (ϵ 1.0×10^3 M^{-1} cm^{-1}) with a Durrum-Gibson stopped-flow spectrophotometer. The experimental conditions are given in Tables I and II. The reaction rate of eq 8 was followed at 245 nm under second-order conditions. Plots of $\ln\{(b_0 - x)/(a_0 - x)\}$ vs. time, where a_0 and b_0 are $[Mo(CN)_8{}^{3-}]_0$ and $[Fe(CN)_6{}^{4-}]_0$, respectively, were linear

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for at least 75% of the reaction. The reaction progress was evaluated from the expression

$$x = \frac{A_t - A_0}{l(\epsilon_3 + \epsilon_4 - \epsilon_1 - \epsilon_2)}$$

where A_t and A_0 represent the absorbance at time t and zero, respectively, ϵ_1, ϵ_2, ϵ_3, and ϵ_4 are the molar absorptivities at 245 nm for $Mo(CN)_8^{3-}$ (ϵ 2.5 × 10^3 M^{-1} cm^{-1}), $Fe(CN)_6^{4-}$ (5.6 × 10^3), $Mo(CN)_8^{4-}$ (1.3 × 10^4), and $Fe(CN)_6^{3-}$ (1.1 × 10^3), respectively, and l is the cell path length (2.00 cm). When the concentrations of the reactants were equal, the rate constants were derived from the slopes of plots of $(A_\infty - A_t)^{-1}$ vs. time, A_∞ being the absorbance at equilibrium. The stoichiometries were evaluated at the selected wavelengths (390 nm for $Mo(CN)_8^{3-}$–benzenediols and 420 nm for $Fe(CN)_6^{3-}$–benzenediols, with excess oxidant; 390 and 245 nm for reaction 8) with a Hitachi Perkin-Elmer spectrophotometer.

Results

Stoichiometry and Kinetics of Benzenediol Oxidation. The spectrophotometric measurements suggest the stoichiometric equation $2Ox + H_2Q \rightarrow 2Red + Q + 2H^+$ (where Q represents the benzoquinone products).

The linearity of first-order plots and the linear dependence of the observed rate constants on the concentration of the benzenediols present in excess, as well as the linearity of the second-order plots, indicate that the reaction rates are all first order in both reactants. Then the rate-determining step is represented by eq 7 for the present systems, followed by

$$Ox + H_2Q^{+}\cdot \xrightarrow{\text{fast}} Red + Q + 2H^+$$

This leads to kinetic expression 9. The specific rate constants k have been collected in Tables I and II.

$$-{}^1/_2 d[Ox]/dt = k[Ox][H_2Q] \tag{9}$$

Stoichiometry and Kinetics of Reaction 8. The spectrophotometric measurements confirmed that reaction 8 is essentially complete as predicted by the reduction potentials of the reactants in the presently investigated conditions (μ = 0.010 M, $NaClO_4$).[17]

A first-order dependence in both reactants was observed, and the second-order rate constant was evaluated by averaging the results of ten different runs (with $[Mo(CN)_8^{3-}]$ and $[Fe(CN)_6^{4-}]$ ranging from 0.5 to 2 × 10^{-5} M): k = (1.2 ± 0.2) × 10^6 M^{-1} s^{-1}, at 25.0 °C, μ = 0.010 M, $NaClO_4$.

Discussion

The same thermodynamic treatment as previously described[5a] was applied to the oxidation of benzenediols by octacyanomolybdate(V) and hexacyanoferrate(III). For $Mo(CN)_8^{3-}$, λ_{12} = 21 kcal mol^{-1} and for $Fe(CN)_6^{3-}$, λ_{12} = 30 kcal mol^{-1} were found to satisfy the experimental results (see Tables I and II); these values lead to $\Delta G^{**}(Mo(CN)_8^{3-/4-})$ = 4.0 kcal mol^{-1}[18] and $\Delta G^{**}(Fe(CN)_6^{3-/4-})$ = 8.5,[20] if $\Delta G^{**}(IrCl_6^{2-/3-})$ is taken as reference.

By calculating now the rate constant for reaction 8 with these values of ΔG^{**} according to eq 2–5 and by computing the work term with the aid of eq 6, the value 1.0 × 10^6 M^{-1} s^{-1} is obtained,[17] to be compared with the experimental 1.2 × 10^6 M^{-1} s^{-1}. Therefore, although the present agreement might be fortuitous, the described method for estimating ΔG^{**} seems to be satisfactory and eq 6 gives acceptable values for the work terms up to 0.010 M ionic strength.

An attempt can be made to use the present values of ΔG^{**} to estimate the rate constant obtained at 0.50 M H_2SO_4 (k = 3.0 × 10^4 M^{-1} s^{-1}).[15] The following values can be obtained with different assumptions:[22] k_{calcd} = 1.4 × 10^7 M^{-1} s^{-1} (by neglecting the work term); 4.9 × 10^6 (w_{12} calculated with eq 6); 1.5 × 10^3 (w_{12} calculated neglecting any ionic strength correction); 8.3 × 10^4 (w_{12} "averaged").[4] It appears that only the last approach gives moderate agreement with the experimental data.

Besides, since in the literature the data concerning the oxidation of $Fe(CN)_6^{4-}$ by $IrCl_6^{2-}$, both in 0.50 M $HClO_4$ and in a medium with no acid and other salts added,[23] are available, it is interesting to compare these data with the aid of eq 2–5 and of the intrinsic parameters presently determined (particularly taking into account that $IrCl_6^{2-/3-}$ has been adopted as a reference system for ΔG^{**}).

With no other electrolytes present, we have used the zero ionic strength extrapolation for computing the work terms: thus, a value k_{calcd} = 1.2 × 10^6 M^{-1} s^{-1} is derived,[24] the same value that was experimentally determined.[23]

In 0.50 M $HClO_4$, if the "averaged" method[4] is adopted, k_{calcd} = 6.2 × 10^5 M^{-1} s^{-1},[25] to be compared with 4.1 × 10^5 M^{-1} s^{-1} experimentally determined.[23] Other methods for computing or neglecting the work terms give calculated rate constants which are 1–2 orders of magnitude different from the experimental one.

From the presently reported examples,[26] the importance of the work terms in the applications of eq 2 to the electron-transfer rate calculations is evident; moreover, comparison of the reaction rates for different oxidants with benzenediols (or other uncharged molecules) can provide a useful source of ΔG^{**} values.

Registry No. $Mo(CN)_8^{3-}$, 17845-99-7; $Mo(CN)_8^{4-}$, 17923-49-8; $Fe(CN)_6^{3-}$, 13408-62-3; $Fe(CN)_6^{4-}$, 13408-63-4; 2-methylbenzene-1,4-diol, 95-71-6; benzene-1,4-diol, 123-31-9; 2-chlorobenzene-1,4-diol, 615-67-8; 4-methylbenzene-1,2-diol, 452-86-8; 4-*tert*-butylbenzene-1,2-diol, 98-29-3; benzene-1,2-diol, 120-80-9.

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(9) The rate constants of electron exchange between radicals and parent molecules have been found to fall in a narrow range for several systems.[10] Besides, the reaction rates of benzoquinones and their anion radicals are almost invariant with structure.[11] It must also be taken into account that, even if some slight differences would be present in the self electron transfers of our systems ($H_2Q^{+}\cdot/H_2Q$), these different intrinsic parameters should introduce the same deviation in the estimated λ_{12}'s, with no influence on $\Delta\lambda_{12}$.
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Evidence of the Higher Order Spin Coupling in an Antiferromagnetic Oligomer Complex

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Received August 29, 1977

The magnetic susceptibility measurement of the dimeric complex of iron $[FeS_4C_4(CF_3)_4]_2$ has been reported by Dance together with the theoretical account for the observations.[1] The dimerization of this oligomeric complex occurs through the two Fe–S bonds bridging the two equivalent monomeric $[FeS_4C_4(CF_3)_4]$ chelate units. Assuming that this oligomer bonding utilizes a sulfur lone pair of electrons and an empty orbital at iron, the number of singly occupied orbitals at each submolecule must be even. Accordingly, each submolecule is supposed to have a spin of 1. However, the usual Heisenberg-type exchange Hamiltonian between two submolecule spins S_a and S_b ($S_a = S_b = 1$) has turned out to be inappropriate to account for the experimental data.

The theoretical model, in which two singly occupied orbitals at each submolecule are involved and all exchange interactions for the four electrons are explicitly included, has been proposed by Dance.[1] Possible sets of the exchange parameters J_{ij} between two electrons each located on the orbitals i and j were derived reproducing well the χ_M–T data. This fact, however, may not necessarily give a basis for withdrawal of the exchange model between submolecule spins S_a and S_b.

In the general theory of the exchange interaction for a many-electron system,[2,3] there has been pointed out that besides the bilinear Heisenberg-type exchange interaction, the higher order spin coupling such as a type among the three spins $(s_i{\cdot}s_j)(s_j{\cdot}s_l)$ or a type among the four spins $(s_i{\cdot}s_j)(s_l{\cdot}s_m)$ etc. can be obtained successively as a series expansion of the energy eigenvalue with regard to the overlap integrals between atomic wave functions. For spins of $^1/_2$, the so-called biquadratic exchange interaction reduces to a bilinear one by eq 1.

$$(s_i{\cdot}s_j)^2 = {}^3/_{16} - {}^1/_2(s_i{\cdot}s_j) \qquad (1)$$

Let the singly occupied orbitals at each submolecule be ψ_1, ψ_2 and ψ_1', ψ_2' and the corresponding spin operators be s_1, s_2 and s_1', s_2', respectively. Then, from the general theory we may have the Hamiltonian

$$\begin{aligned} H = {} & -2K_0\{(s_1{\cdot}s_2) + (s_1'{\cdot}s_2')\} - 2K_1\{(s_1{\cdot}s_1') + (s_1{\cdot}s_2') + \\ & (s_2{\cdot}s_1') + (s_2{\cdot}s_2')\} - K_2'\{(s_1{\cdot}s_1')(s_1{\cdot}s_2') + \\ & (s_2{\cdot}s_1')(s_2{\cdot}s_2') + (s_1{\cdot}s_1')(s_2{\cdot}s_1') + (s_1{\cdot}s_2')(s_2{\cdot}s_2') + \\ & \mathrm{HC}\} - K_2''\{(s_1{\cdot}s_1')(s_1{\cdot}s_2) + (s_1{\cdot}s_2)(s_2{\cdot}s_2') + \\ & (s_1{\cdot}s_1')(s_1'{\cdot}s_2') + (s_2{\cdot}s_2')(s_2'{\cdot}s_1') + \mathrm{HC}\} - \\ & K_2'''\{(s_1{\cdot}s_2)(s_1{\cdot}s_2') + (s_1{\cdot}s_2)(s_2{\cdot}s_1') + (s_2{\cdot}s_1')(s_1'{\cdot}s_2') + \\ & (s_1{\cdot}s_2')(s_2'{\cdot}s_1') + \mathrm{HC}\} - 2K_3\{(s_1{\cdot}s_1')(s_2{\cdot}s_2') + \\ & (s_1{\cdot}s_2')(s_2{\cdot}s_1')\} - 2K_3'(s_1{\cdot}s_2)(s_1'{\cdot}s_2') \end{aligned} \qquad (2)$$

where HC denotes the part of Hermitian conjugate. The two terms of mutually Hermitian conjugate can be reduced to a bilinear term by using the relation

$$(s_i{\cdot}s_j)(s_i{\cdot}s_k) + (s_i{\cdot}s_k)(s_i{\cdot}s_j) = {}^1/_2(s_j{\cdot}s_k) \qquad (3)$$

If we assume that $K_2'' = K_2'''$ and neglect the term of K_3', eq 2 can be rewritten as

$$\begin{aligned} \tilde{H} = {} & -(2K_0 + K_2')\{(s_1{\cdot}s_2) + (s_1'{\cdot}s_2')\} - (2K_1 + \\ & K_2'')\{(s_1{\cdot}s_1') + (s_1{\cdot}s_2') + (s_2{\cdot}s_1') + (s_2{\cdot}s_2')\} - \\ & 2K_3\{(s_1{\cdot}s_1')(s_2{\cdot}s_2') + (s_1{\cdot}s_2')(s_2{\cdot}s_1')\} \end{aligned} \qquad (4)$$

With the spin operators S_a and S_b which are defined as

$$S_a = s_1 + s_2 \qquad S_b = s_1' + s_2' \qquad (5)$$

eq 4 can further be simplified as

$$H = -2J(S_a{\cdot}S_b) - 2J'(S_a{\cdot}S_b)^2 \qquad (6)$$

In other words, the Hamiltonian for the present four-electron system will generally be given by the customary Heisenberg exchange interaction and the biquadratic one between the submolecule spins S_a and S_b.

The calculation of the molar susceptibility χ_M for the Hamiltonian (eq 6) can be done straightfowardly using the vector model.[4] The spin states have total spin $S' = S_a + S_b$ ($S' = 0, 1, 2$) with relative energies $E(S')$. For the antiferromagnetic sign of J, we have the ground state $S' = 0$, $E(0) = 0$ and the excited states $S' = 1$, $E(1) = -2J + 6J'$ and $S' = 2$, $E(2) = -6J + 6J'$. The experimental data will be compared with the well-known susceptibility formula

$$\chi_M = \frac{Ng^2\mu_B{}^2}{3kT}\,\frac{\sum\limits_{S'} S'(S'+1)(2S'+1)\exp[-E(S')/kT]}{\sum\limits_{S'}(2S'+1)\exp[-E(S')/kT]} + \chi_{\mathrm{const}} \qquad (7)$$

where N is Avogadro's number, g is the g factor, μ_B is the Bohr magneton, and χ_{const} represents both the Van Vleck high-frequency part and the diamagnetic contributions of the magnetic susceptibility.

With the use of the FACOM 230-75 computing facility, the temperature dependence of the susceptibility has been calculated for various sets of values of parameters in the ranges of −200 to −250 cm^{-1} for J and −40 to −70 cm^{-1} for J', taking $g = 2.00$. For no positive values of parameters will this model reproduce the observations. We could find several sets of values which show an excellent agreement with Dance's data. In Figure 1, the calculation for the case (A) $J = -210$ cm^{-1}, $J' = -53$ cm^{-1}, $\chi_{const} = -500 \times 10^{-6}$ cgsu is shown and compared with the experimental data. The other set of values, for example (B) $J = -220$ cm^{-1}, $J' = -56$ cm^{-1}, $\chi_{const} = -430 \times 10^{-6}$ cgsu or (C) $J = -225$ cm^{-1}, $J' = -58$ cm^{-1}, $\chi_{const} = -500 \times 10^{-6}$ cgsu, also gives a nice fitting with the observations. The theoretical curves for the cases (B) and (C) practically coincide with the curve in Figure 1. Therefore, it may be concluded that the present simple model is quite useful to account for the magnetic behaviors of the oligomer complex of iron and is equally significant as the more complicated theoretical