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Nonlocal Medium Effects on the Temperature Dependence of Electron-Transfer Rate Constants

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According to recent formulations of the rate theory of chemical processes,[1,2] the temperature dependence of the rate constant, k, of elementary electron- and atom-group-transfer processes arises primarily from the following causes.

(A) At high temperatures, when $k_BT/\hbar$ is larger than all vibrational frequencies of the system (where k_B is Boltzmann's constant, T is the absolute temperature, and $\hbar = h/2\pi$, where h is Planck's constant), all modes behave classically; i.e., they are displaced from their initial to their final equilibrium configuration by thermally activated motion and therefore provide an Arrhenius temperature-dependent rate constant.[1,2] At intermediate temperatures the major part of the solvent modes are thermally activated and contribute to the apparent activation energy,[1,3,4] while the intramolecular modes of the reactants[1,2] and the high-frequency part of the solvent modes are frozen.[3,4] At still lower temperatures an increasing fraction of the low-frequency medium modes also become frozen leading eventually to a temperature-independent rate constant.[5] Studies of electron- and atom-group-transfer processes in biological systems[6-10] and of proton- and hydrogen-atom-transfer processes involving small molecular reactants[11-13] have provided experimental evidence for these effects. In contrast, low-temperature (195–298 K) studies of the $Fe^{3+/2+}$-exchange reaction in acid aqueous solutions showed that this process was apparently first order in each reactant and had a constant activation energy in the whole temperature interval, even though a phase transition from a liquid to a glass occurred at 215 K.[14,15] This result is remarkable, as it is not consistent with immobile reactants in the solid and hard to reconcile with Debye relaxation providing a substantial part of the activation energy in the liquid phase such as is commonly accepted.

(B) The temperature dependence may also arise from the temperature effect on the short-range order of the medium. The effect of short-range order on the kinetic and thermodynamic parameters is commonly expressed as space dispersion of the dielectric medium.[16] It is physically associated with the interaction between individual solvent molecules inside characteristic correlation lengths, λ, leading to a collective response of the medium molecules to an external field. If the correlation lengths are small compared with all molecular dimensions, the space dispersion can be disregarded. This is inherent in the formalism most commonly applied for the analysis of simple electron-transfer processes. For example, the (Coulomb) work terms, w_r, required to bring the reactants from infinity to their position in the collision complex (separated by a distance R) are commonly written

$$w_r = z_1z_2e^2/\epsilon_sR \qquad (1)$$

where z_1e and z_2e are the charges of the reactants and ϵ_s is the static dielectric constant. The solvent reorganization energy, E_s, is most commonly taken to be[17]

$$E_s = \frac{e^2}{8\pi}\left(\frac{1}{\epsilon_o} - \frac{1}{\epsilon_s}\right)\left(\frac{1}{r_1} + \frac{1}{r_2} - \frac{2}{R}\right) \qquad (2)$$

where r_1 and r_2 are the ionic radii and ϵ_o is the optical dielectric constant. In addition to space dispersion all effects of frequency dispersion[3,4] and finite volume and polarizability[18] of the ions have been ignored in eq 2. If we still ignore the latter effects, eq 1 and 2 are thus appropriate for $\lambda \ll r_1, r_2, R$. If we invoke space correlation in a single mode, e.g., the Debye relaxation motion, i.e., if we let $\lambda > r_1, r_2, R$, then eq 1 and 2 take the form[16b,c]

$$w_r = \frac{z_1z_2e^2}{\epsilon_s{}^R}\left[\frac{1}{\epsilon_1} - \left(\frac{1}{\epsilon_1} - \frac{1}{\epsilon_s}\right)\left(\tilde{F}\left(\frac{r_1}{\lambda},\frac{r_2}{\lambda},\frac{R}{\lambda}\right)\right)\right] \qquad (3)$$

$$E_s = \frac{e^2}{8\pi}\left(\frac{1}{\epsilon_o} - \frac{1}{\epsilon_s}\right) \times \left[\frac{1}{r_1}\left(F\left(\frac{r_1}{\lambda}\right)\right) + \frac{1}{r_2}\left(F\left(\frac{r_2}{\lambda}\right)\right) - \frac{2}{R}\left(\tilde{F}\left(\frac{r_1}{\lambda},\frac{r_2}{\lambda},\frac{R}{\lambda}\right)\right)\right] \qquad (4)$$

where ϵ_1 is the dielectric constant of the transparency band on the high-frequency side of the modes subject to space-dispersion effects (corresponding to the infrared polarization, i.e., $\epsilon_1 \approx 4$ for water). The exact form of $F(x)$ and $\tilde{F}(x)$ depends on the particular functional appearance of the correlation functions. Generally, however, $F(x) \to 1$ for $x \to \infty$ and $F(x) \to 0$ for $x \to 0$. Similarly, $F(x,y,z) \to 1$ and 0 for $x, y, z \to \infty, \infty, \infty$ and 0, 0, 0, respectively. Space-correlation effects will thus give larger values of w_r and smaller values of E_s than those estimated without incorporating these effects. Since the correlation effects are physically associated with the liquid structure, λ, and therefore the activation energy, may well display a considerable temperature dependence.

We shall illuminate the disentanglement of the various origins of the temperature dependence of the rate constant by considering a particular electron-transfer reaction in different media. The process is[19]

$$[Co(NH_3)_5H_2O]^{3+} + [Ru(NH_3)_6]^{2+} \to [Co(NH_3)_5H_2O]^{2+} + [Ru(NH_3)_6]^{3+} \qquad (5)$$

This choice was dictated by: (a) a rate constant of a convenient magnitude; (b) a large equilibrium coordinate shift in a single "high-frequency" mode [while the nuclear coordinate displacements in the Co(III)/Co(II) couple are not known, the metal–ligand bond lengths in the $[Co(NH_3)_6]^{3+/2+}$ couple are displaced by 0.16 Å;[20] in comparison, the displacement of the Ru–NH_3 bonds are only 0.04 Å.[21]]; (c) an intramolecular mode of such a frequency that its thermal excitation is changed significantly around room temperature [numerical calculations show that frequencies in the range 800–1200 cm^{-1} are most favorable for the possible observation of the "freezing effect" around room temperature;[22] the frequencies of the Co complex (500 and 350 cm^{-1} for $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_6]^{2+}$, respectively[23]) are largely classical at room temperature, but the activation energy is still expected to decrease by up to 10% from this effect when the temperature is decreased by 80–100 K].

$[Co(NH_3)_5H_2O]Cl_3$ and $[Ru(NH_3)_6]Cl_2$ were prepared by literature procedures[24] and checked spectrophotometrically.[25] Doubly distilled water was used throughout, and all other materials were analytical grade and used without further purification. The reaction media were 68:32 w/w methanol/water and 67:37 ethylene glycol/water. No crystallization or glass transition occurs in the temperature range investigated. $[Ru(NH_3)_6]^{2+}$ was found to react slowly with both methanol and ethylene glycol, but the much faster reaction of Ru(II) with Co(III) was apparently not affected by this. The ionic strength (0.2 mol dm^{-3}) and pH 1.0 were adjusted with a mixture of trifluoroacetic acid and its sodium salt. The reaction was first order in each reactant in the concentration range (2–7) × 10^{-3} mol dm^{-3} and followed spectrophotometrically by monitoring Co(III) (in excess) directly in a thermostated quartz cell or by removing samples, quenching with acid solutions of iron(III) chloride, and determining

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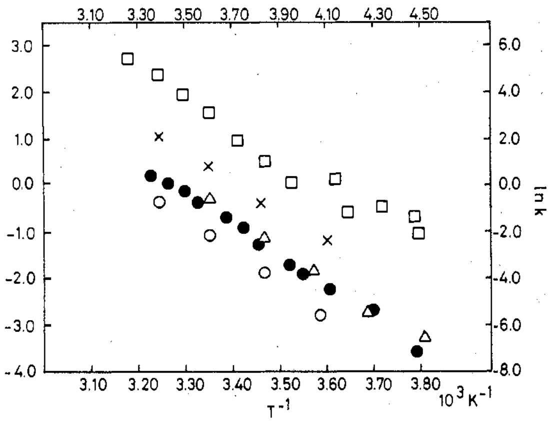

Figure 1. Plots of log k (dm^3 mol^{-1} s^{-1}) against T^{-1}: □, ethylene glycol–0.1 M HCl; △, ethylene glycol–CF_3COOH; ●, methanol–CF_3COOH; ×, water–0.1 M HCl; ○, water–CF_3COOH; top and right-hand scale, methanol; bottom and left-hand scale, ethylene glycol and water.

Table I. Rate Parameters in the Limits of High ("h") and Low ("l") Temperatures[a]

medium	k	E_A	H_A	S_A	G_A
eth–0.1 M HCl, "h"	4.84	63 ± 1	61 ± 1	−28 ± 4	69 ± 2
eth–CF_3COOH, "h"	0.76	60 ± 1	57 ± 1	−64 ± 4	76 ± 2
eth–0.1 M HCl, "l"		33 ± 5	31 ± 5	−134 ± 20	70 ± 6
eth–CF_3COOH, "l"		50 ± 3	48 ± 3	−90 ± 10	74 ± 6
meth–CF_3COOH	1.58	56 ± 1	53 ± 1	−61 ± 2	72 ± 2
H_2O–0.1 M HCl	1.54	53 ± 1	51 ± 1	−76 ± 4	76 ± 3
H_2O–CF_3COOH	1.54	61 ± 1	58 ± 1	−59 ± 3	76 ± 3

[a] k in dm^3 mol^{-1} s^{-1} (25 °C); E_A, H_A, and G_A in kJ; S_A in J K^{-1}. Abbreviations: eth, ethylene glycol/water; meth, methanol/water.

Co(III) spectrophotometrically. The temperature of the reaction mixture was measured directly by a chromel/alumel thermocouple, and all reactions proceeded in an atmosphere of argon which had previously passed solutions of chromium(II) chloride and a cooling trap. The lower limits of the temperatures were determined by the difficulty of mixing the solutions (ethylene glycol) or by the extremely low rate of reaction (methanol).

Figure 1 shows plots of log k against T^{-1}, and Table I summarizes the room-temperature and low-temperature limiting values of the activation parameters. The most striking result is that the plot for the methanol solution is linear over about 80 K while the plot for the ethylene glycol solutions displays a pronounced curvature already at fairly high temperatures. These effects may arise from the following causes.

(1) The Freezing of the Metal–Ligand Stretching Modes of the Co(III) Complex with Decreasing Temperature. This can be excluded, however, since the effect is far higher than compatible with any reasonable structural and spectroscopic parameter values for the Co(III) complex and since it is only observed for the ethylene glycol mixture. The latter reason also implies that the effect is not likely to be caused by the freezing of solvent modes such as hindered translation or rotation (in the frequency range 500–700 cm^{-1} for water[26]).

(2) Immobilization of the Reactants at Lower Temperatures. The viscosity of the ethylene glycol solution increases by a factor of about 5–10 in the temperature range investigated.[27] However, the diffusion coefficients of the reactants would then still only be about 20 times lower than in water at room temperature. The effect is therefore not likely to involve diffusion control or electron transfer between fixed reactants.

(3) The Possibility That Activation Energy May Finally Decrease due to an Increasing Order (Increasing Correlation Length) in the Liquid. We can illustrate this further in the following semiquantitative terms. The semiclassical rate expression is[1,28]

$$k = \varkappa \frac{\omega_{\text{eff}}}{2} \Delta V \times \exp\{-[w_r + (E_s + E_r + \Delta G_0)^2/4(E_s + E_r)]k_B T\} \quad (6)$$

where E_r is the intramolecular reorganization energy, $\varkappa$ the transmission coefficient, ω_{eff} the "effective" frequency, ΔV the volume of the reaction zone, and ΔG_0 the free energy of reaction. k can be written in terms of absolute rate theory

$$k = (k_B T/h) \exp(-G_A/k_B T) \quad (7)$$

where the free energy of activation, G_A, is now

$$G_A = w_r + (E_s + E_r + \Delta G_0)^2/4(E_s + E_r) - k_B T \ln \left(\varkappa \frac{h\omega_{\text{eff}}}{k_B T} \Delta V \right) \quad (8)$$

The activation enthalpy, H_A, is then formally

$$H_A = G_A - T(\mathrm{d}G_A/\mathrm{d}T) \quad (9)$$

If we insert eq 8 into eq 9 and notice (see below) that $\Delta G_0 \ll E_s, E_r$, then

$$H_A = w_r + \frac{E_s}{4} + \frac{E_r}{4} + \frac{\Delta G_0}{2} - T(\mathrm{d}w_r/\mathrm{d}T - \mathrm{d}E_s/\mathrm{d}T) + k_B T(\mathrm{d} \ln \varkappa/\mathrm{d}T) \quad (10)$$

Anticipating the outcome of our discussion, we have included a temperature dependence of the transmission coefficient. This is plausible in view of the fact that an increasing correlation length causes an increasing w_r,[16b] which again implies that the reactants are pushed further apart. We notice further that if $\mathrm{d}w_r/\mathrm{d}T$ and $\mathrm{d}E_s/\mathrm{d}T$ are approximately constant, then

$$H_A(T) \approx H_A(T_0) + k_B T \ln \varkappa(T)/\varkappa(T_0) \quad (11)$$

while

$$G_A(T) \approx G_A(T_0) + (\mathrm{d}w_r/\mathrm{d}T)\Delta T + \tfrac{1}{4}(\mathrm{d}E_s/\mathrm{d}T)\Delta T - k_B T \ln \varkappa(T)/\varkappa(T_0) \quad (12)$$

where $\Delta T = T - T_0$. In other words, the difference in H_A at two different temperatures is solely reflected in $\varkappa(T)$, while the temperature dependence of G_A arises from w_r, E_s, and $\varkappa(T)$.

The experimental data now show (Table I) that $H_A(T) - H_A(T_0) \approx 30$ and 10 kJ for hydrochloric and trifluoroacetic acid media, respectively, while $G_A(T) - G_A(T_0) \approx 0$ in both cases. T and T_0 refer here to the lower limit of the temperature interval investigated and the high-temperature (linear) branch of the Arrhenius plot, respectively. Furthermore, in the range where the Arrhenius plot is linear, E_s, estimated from the experimental value of G_A and the spectroscopic[23] and thermodynamic[19,29] data for the Co and Ru complexes, $\varkappa = 1$ and $\Delta V = 1$ mol dm^{-3},[30] is 125–150 kJ, which is very close to the value calculated from eq 2 (125 kJ). This suggests that correlation effects may be ignored in the high-temperature limit. We can then estimate $\varkappa(T)/\varkappa(T_0) \approx \varkappa(T) \approx 10^{-6}$–$10^{-5}$ and 10^{-3}–10^{-2} for the two different ionic media; i.e., at the lower temperatures the increased order of the medium induces a longer electron-transfer distance and a correspondingly smaller transmission coefficient. This is associated with the very high sensitivity of w_r to the correlation length (higher than the sensitivity of E_s) which pushes the ions apart in order to avoid the large contribution of w_r to the activation energy at the lower temperatures.

The effect of the smaller transmission coefficient is compensated by a smaller E_s. w_r is subject to an increase from the increased correlation length of the liquid but also to a substantial decrease from the larger electron-transfer distance. If we assume that these two effects cancel each other, E_s becomes smaller at the lower temperatures by about 120 and

38 kJ for the two ethylene glycol media. These values can be associated with given correlation lengths if we invoke a given functional form for the medium-dipole correlation functions. If the correlation between the dipoles can be represented by an exponentially decaying function of decay length λ, this provides well-defined tractable expressions for $F(x)$ and $\tilde{F}(x)$,[16] from which E_s can be calculated for given values of λ. Following this procedure, a value of $\lambda \approx 1.5r \approx 4$ Å is necessary to reproduce the "experimental" change in E_s.

Introduction of a temperature-dependent correlation length which describes the increasing organization of the medium with decreasing temperature can thus account for the observed effects for reasonable values of the appropriate correlation length. Our approach also shows that when rate constants are measured over large temperature intervals, all the effects considered above must be invoked, but a proper choice of system (e.g., electrically neutral reactants) may well provide reasonable estimates of their individual contributions.

Registry No. $[Co(NH_3)_5H_2O]^{3+}$, 14403-82-8; $[Ru(NH_3)_6]^{2+}$, 19052-44-9; $[Co(NH_3)_5H_2O]^{2+}$, 22045-50-7; $[Ru(NH_3)_6]^{3+}$, 18943-33-4.

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X-ray Crystal and Molecular Structure of Tris(*N*,*N*-diethyldithiocarbamato)-bis[μ-(*N*,*N*-diethyltrithiocarbamato)]-diosmium(III) Tetraphenylborate. The First Example of a Sulfur-Rich Dithiocarbamate

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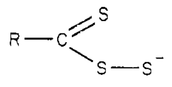
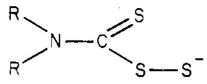
Examples of metal complexes which contain sulfur-rich dithiocarboxylates or perthiocarboxylates (I, R = aryl or alkyl)



I

as ligands are well-known.[1-4] These complexes are generally formed by the oxidative addition of elemental sulfur or anionic polysulfides to transition-metal dithio acid complexes. Several of these complexes have been characterized by single-crystal X-ray analyses.[1,2] Analogous sulfur-rich N,N-disubstituted dithiocarbamato (II), $^-S_3CNR_2$, complexes have not been



II

observed,[5] although there has been considerable interest in such species because they are thought to be key intermediates in rubber vulcanization accelerated by zinc dithiocarbamates.[6,7] It has been proposed that perthiocarbamates are the source of the sulfidic cross-links in the vulcanized-rubber matrix.[6,7] During our studies on the structural and redox chemistry of the dithiocarbamato complexes of osmium,[8,9] we isolated crystals of a novel sulfur-rich (*N*,*N*-diethyldithiocarbamato)diosmium complex, $[Os_2(S_2CNEt_2)_3(S_3CNEt_2)_2]BPh_4$. A single-crystal X-ray analysis provides unambiguous evidence for the existence of the trithiocarbamate ligand.

Experimental Section

Crystals of $[Os_2(S_2CNEt_2)_3(S_3CNEt_2)_2]BPh_4$ were isolated as a byproduct in the synthesis of $Os(S_2CNEt_2)_3$ and $[Os_2(S_2CNEt_2)_5]^+$.[8] The actual procedure used varied slightly from the one reported in ref 8. $(NH_4)_2[OsCl_6]$ (2.3 mmol) was reacted with NaS_2CNEt_2 (9.0 mmol) in refluxing $MeOH/H_2O$ (200 mL, 50:50 v/v) under a N_2 atmosphere for 20 h. The brown precipitate was extracted with CH_2Cl_2 and column chromatographed (alumina, Alcoa F-20). Elution with CH_2Cl_2 removed $Os(S_2CNEt_2)_3$ (orange band) in ca. 50% yield based on osmium. The column was then eluted with acetone until the collected fractions were colorless. Finally, elution with methanol removed a brown band. The brown methanol solution was reduced in volume, and upon addition of $NaBPh_4$ a brown precipitate formed. This solid was extracted with CH_2Cl_2 and column chromatographed on alumina. Elution with CH_2Cl_2 removed a brown band which presumably contains a mixture of $[Os_2(S_2CNEt_2)_5]BPh_4$ and $[Os_2(S_2CNEt_2)_3(S_3CNEt_2)_2]BPh_4$. Crystals of the latter were obtained by the vapor-diffusion technique with acetone and ethyl ether. The final yield of this compound was less than 5% on the basis of osmium. None of the crystals were of high quality, and a small elongated rectangular needle (0.10 × 0.05 × 0.02 mm) was used for data collection. The cell constants, $a = 13.595$ (4) Å, $b = 18.492$ (7) Å, $c = 13.320$ (20) Å, $\alpha = 98.68$ (6)°, $\beta = 112.55$ (7)°, and $\gamma = 94.02$ (3)°, were determined by least-squares refinement of the angular settings of 25 Mo Kα ($\lambda = 0.71069$ Å) reflections centered on a CAD 4 diffractometer using the Enraf-Nonius automatic peak-centering

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