Table II. Quenching of $^*Ru(bpy)^{3+}$ by Co(III) Cage Complexes

electron-transfer agent	$E°$, V[d]	$10^{-8}k_q$,[b] $M^{-1}\ s^{-1}$ (acetate buffer, 0.5 M $NaClO_4$)	Φ_{max}[c]	$\Phi_{Co(II)}$[a,b]	$10^{-8}k_2'$, $M^{-1}\ s^{-1}$	k_2'/k_q
$Co^{III}(meoxosar\text{-}H)^{2+}$	−0.59	0.7 (2.8)	0.08	$<10^{-4}$	$<10^{-3}$	
$Co^{III}(COOC_2H_5meoxosar\text{-}H)^{2+}$	−0.53	1.0 (3.6)	0.11	$<10^{-4}$	$<10^{-3}$	
$Co^{III}(sar)^{3+}$	−0.42	0.4 (2.2)	0.05	4×10^{-3}	0.03	0.08
$Co^{III}(NH_2mesar)^{3+}$	−0.36	0.6 (3.3)	0.06	0.01	0.08	0.13
$Co^{III}(Clsar)^{3+}$	−0.29	1.3 (3.0)	0.14	0.05	0.42	0.32
$Co^{III}(sep)^{3+}$	−0.28	1.5 (2.2)[27] (5.5)	0.15	0.04	0.34	0.23
$Co^{III}(azacapten)^{3+}$	−0.05	13.2 (58)	0.62	0.6	12.0	0.89

[a] Same reaction mixture as Table I but in the absence of Pt. [b] k_q and the formation of Co(II), $\Phi_{Co(II)}$, are sensitive to the ionic strength of the solution. No attempt has been made to optimize the H_2 evolved by varying the ionic content. [c] Equal to $k_q[ETA]/(k_q[ETA] + k_1)$. [d] 0.1 M $NaClO_4$.

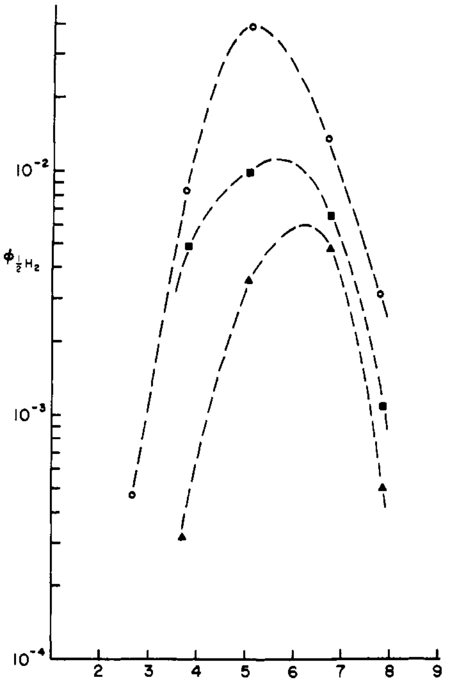

Figure 1. Quantum yield of hydrogen formation as a function of pH for the conditions given in Table I: (○) $Co(sep)^{3+}$; (■) $Co(NH_2mesar)^{3+}$; (▲) $Co(sar)^{3+}$.

5. H_2 is formed quite readily if the reaction mixture (pH 5) is connected electrochemically to an acidic solution (pH 0) with Pt electrodes.

The quantum yield of hydrogen formation $\Phi_{1/2H_2}$ as a function of pH is plotted in Figure 1. The maximum rate is at pH 5 for $Co(sep)^{3+}$, whereas for $Co(sar)^{3+}$, it is near pH 6. Since $\Phi_{1/2H_2}$ (pH 5) is nearly equal to $\Phi_{Co(II)}$ (Table II), reaction 5 must be very efficient for these complexes.

If we consider the rate of hydrogen formation by using Pt as catalyst, mv^{2+} is a better electron-transfer agent than the Co(III) complexes (Table I). However, with other metal oxides the performance of mv^{2+} is worse. For example, if colloidal RuO_2 dispersed in silica (5×10^{-5} M Ru) is used as catalyst[34,35] and the reaction mixture is normalized to 1-L volume, the rate of H_2 formation for $Co(Clsar)^{3+}$ is 55 μmol min^{-1} but with mv^{2+} the rate is only 11 μmol min^{-1} under identical experimental conditions. With RuO_2 as catalyst the driving force of $mv^{+}\cdot$ ($\Delta G \approx -0.14$ V at pH 5) is insufficient to reduce water effectively and $mv^{+}\cdot$ accumulates in the reaction mixture. Despite $\Delta G \approx +0.01$ V $(Co(Clsar))^{2+}$ forms hydrogen quite readily.

Analysis by HPLC[36] shows that the Co(II) cage complexes have turnover numbers for the formation of hydrogen at least two orders of magnitude higher than that of mv^{2+}, but aspects of the ease of electron transfer (k_2) and the degree of separation in this process need further investigation.

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Registry No. $Co(meoxosar)^{2+}$, 85664-20-6; $Co(COOH_2H_5meoxosar)^{2+}$, 85664-18-2; $Co(sar)^{3+}$, 85664-13-7; $Co(NH_2mesar)^{3+}$, 85663-97-4; $Co(Clsar)^{3+}$, 85663-92-9; $Co(sep)^{3+}$, 72496-77-6; $Co(azacapten)^{3+}$, 81505-65-9; $Ru(bpy)_3^{2+}$, 15158-62-0; Pt, 7440-06-4; H_2, 1333-74-0; edta, 60-00-4.

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(35) Prepared by depositing $RuCl_3$ (Fluka) on spherical SiO_2 particles (average diameter 40 Å) called Nalcoag 1115 from Nalco Chemical Co., Oak Brook, IL 60521.

(36) Conditions as in ref 21 but eluent was an aqueous solution of THF (10%), CH_3COOH (1%), sodium heptasulfonate nonahydrate (0.08%), and methanesulfonic acid (0.02%), neutralized to pH 3.1 with tetramethylammonium hydroxide.

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Ionic Strength Dependence of the Volume of Activation for Reactions between Ions

Sir:

The study of inorganic substitution reactions through the measurement of volumes of activation has recently become an active field of research.[1] Several research groups are now extending these studies to electron-transfer reactions.[2] Since the molal volumes of ions are strongly dependent on solvent electrostriction, which in turn is influenced by the ionic strength of the medium,[3] it is important to consider the influence of ionic strength on volumes of activation. This paper presents the expression for the dependence of the volume of activation on ionic strength, which is analogous to the typical

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0020-1669/83/1322-2349$01.50/0

expression for the ionic strength dependence of the rate constant. This is a correction to a commonly applied equation presented by Stranks[4] for the analysis of outer-sphere electron-transfer reactions.

The most commonly used equation for the ionic strength dependence of the bimolecular rate constant is[5,6]

$$\ln k = \ln k^0 + 2Z_1Z_2\left(\frac{CI_m^{1/2}}{1 + BaI_m^{1/2}}\right) \tag{1}$$

$$C = (2\pi N_0\rho)^{1/2}\left(\frac{e^2}{4\pi\epsilon_0\epsilon k_B T}\right)^{3/2} \tag{2}$$

$$B = e\left(\frac{2N_0\rho}{\epsilon_0\epsilon k_B T}\right)^{1/2} \tag{3}$$

where k^0 is the rate constant at infinite dilution, Z_1 and Z_2 are the charges on the reactants, a is the distance of closest approach between reactants and their counterions (m), I_m is the molal ionic strength, N_0 is Avogadro's number, ρ is the density of the solvent (kg/m^3), e is the charge on the proton, ϵ_0 is the permittivity of a vacuum, ϵ is the dielectric constant of the solvent, k_B is Boltzmann's constant, and T is the absolute temperature. The equation is derived from the Debye–Hückel expression for the molal activity coefficients of the reactants and the transition state, in SI units. From transition-state theory

$$\Delta V^{\ddagger} = -RT\left(\frac{\partial \ln k}{\partial P}\right)_T \tag{4}$$

where R is the gas constant and P is the pressure (Pa). The two physical properties in these equations that are pressure dependent are ϵ and ρ. With the substitution for the compressibility of the solvent, κ

$$\kappa = \left(\frac{\partial \ln \rho}{\partial P}\right)_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{5}$$

the expression for $\Delta V^{\ddagger}$ becomes

$$\Delta V^{\ddagger} = -RT\left(\frac{\partial \ln k^0}{\partial P}\right)_T + \left(\frac{RTZ_1Z_2CI_m^{1/2}}{(1 + BaI_m^{1/2})^2}\right)\left[\left(\frac{\partial \ln \epsilon}{\partial P}\right)_T(3 + 2BaI_m^{1/2}) - \kappa\right] \tag{6}$$

The most significant difference between this equation and that of Stranks is that the sign of the ionic strength dependent term is changed. It can be seen qualitatively that this is the proper sign, since the increase of ionic strength produces a screening effect that decreases electrostriction and increases molal volumes. The effect is more extreme for a transition state with a higher charge density than that of the reactants. Thus, the correction should have a positive sign in a reaction between like-charged ions (vide infra). Substitution of the constants for the case of water at 298 K [$C = 1.174$ (kg/mol)$^{1/2}$, $B = 3.284$ (kg/mol)$^{1/2}$ m^{-1}, $\kappa = 4.52 \times 10^{-10}$ Pa^{-1},[7] $(\partial \ln \epsilon/\partial P)_T = 4.71 \times 10^{10}$ Pa^{-1},[8] $R = 8.315 \times 10^6$ cm^3 Pa mol^{-1} K^{-1} so that $\Delta V^{\ddagger}$ has the units cm^3/mol] and the conditions of I_m of 0.1 m and a radius of 4×10^{-10} m give

$$\Delta V^{\ddagger}\ (\text{cm}^3/\text{mol}) = (2.48 \times 10^9)\left(\frac{\partial \ln k^0}{\partial P}\right)_T + 0.62(Z_1Z_2) \tag{7}$$

A case considered by Stranks[4] both theoretically and experimentally is the outer-sphere electron self-exchange of $\mathrm{Co(en)_3}^{2+/3+}$ (en is 1,2-ethanediamine) at 65 °C in 0.5 m ionic strength aqueous solution and with $a = 4.1 \times 10^{-10}$ m. The calculated value for the ionic strength dependent term is 6.5 cm^3/mol, which is to be compared with the value of −4.4 cm^3/mol given by Stranks. Combined with the other terms in the total expression presented by Stranks, which is derived from the Hush theory for outer-sphere electron-transfer reactions, this gives a predicted $\Delta V^{\ddagger}$ of −7.5 cm^3/mol. This compares to the measured value of −19.8 ± 1.5 cm^3/mol. The apparent agreement of the previously calculated value, −18.4 cm^3/mol, with the measured value is one of the reasons that $\Delta V^{\ddagger}$ measurements have not been pursued for simple outer-sphere electron-transfer systems. It is now clear that the measured value is significantly more negative than is predicted. Possible origins for this deviation include use of the activity coefficient expression at too high an ionic strength, imprecision of the model that treats the solvent as a dielectric continuum, treats the reactants as uniformly charged spheres, and ignores ion pairing, and the ignoring of the nuclear and especially the electronic transmission coefficient[9] variation with pressure. The first concern is not sufficient since even the k^0 term has too positive a $\Delta V^{\ddagger}$ value. The model may be improved, but it is difficult to consider a molecular instead of a continuum solvent.[10] Use of the currently popular Marcus theory expressions and the work term treatment for the electrostatic interactions,[11] which are also based on the Debye–Hückel theory, gives a result quite similar to the corrected Stranks result. The complex problem of the preexponential transmission coefficient factors, which include the question of adiabaticity of the slow $\mathrm{Co(en)_3}^{2+/3+}$ electron self-exchange reaction, is worthy of consideration.

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