oxidase activity.[8,9] The value of K_m^{Cl}, which was determined to be 344 mM at pH 5, indicates that V–Br(PO) has a much lower affinity for chloride than bromide (i.e., K_m^{Br} = 10 mM at pH 5[9]). The V–Br(PO) pH optima for chloroperoxidase activity was found to be pH 5, which is the same for bromoperoxidase activity.[9,16] In contrast, the Fe heme bromoperoxidase isolated from the marine green alga *Penicillus capitatus* catalyzes the oxidation of bromide with optimum activity at pH 6 and the oxidation of chloride with optimum activity at pH 4,[17] although like the case for the vanadium enzyme, the chloroperoxidase activity is much less than the bromoperoxidase activity.[17,18] The substantially lower chloroperoxidase activity of V–Br(PO) reflects, in part, the smaller driving force for chloride oxidation by hydrogen peroxide than bromide oxidation but also the difference in K_m values for the halides.

In the absence of an organic substrate, V–Br(PO) catalyzes the chloride-assisted disproportionation of hydrogen peroxide, forming dioxygen as measured by an oxygen electrode. The rate of dioxygen formation is equal to the rate of MCD chlorination (Table I), suggesting that the rate-limiting step for both reactions is the formation of a common intermediate (e.g., the oxidized chloride species) analogous to the reactions with bromide (see scheme, above).[9] The rate of the chloride-assisted dioxygen formation is inhibited by amines (e.g., taurine; Table I), which is consistent with chloramine formation, since hydrogen peroxide cannot reduce chloramine to form dioxygen and chloride.[19] By contrast, the bromide-assisted disproportionation of hydrogen peroxide is not inhibited by amines because hydrogen peroxide rapidly reduces bromamine compounds, forming singlet oxygen.[3,19] Consequently, the rates of MCD bromination and bromide-assisted disproportionation of hydrogen peroxide (in the absence of MCD) are equal independent of the presence of amine.[3,9] The rate of MCD chlorination is not inhibited by taurine (Table I).

Previously proposed mechanisms of the biosynthesis of certain chlorinated compounds have invoked electrophilic bromination of alkenes followed by passive chloride attack.[6] While this mechanism could explain the origin of adjacent brominated and chlorinated carbons, it does not readily account for chlorine-only-containing compounds. Thus, with the discovery of chloroperoxidase activity of the vanadium enzyme, the origin of specific chlorinated marine natural products can now be addressed. We are continuing to investigate the mechanism and substrate selectivity of chlorination catalyzed by V–Br(PO) to ascertain whether this abundant marine vanadoenzyme should be termed *vanadium chloroperoxidase*.

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(16) de Boer, E.; Wever, R. *J. Biol. Chem.* **1988**, *263*, 12326–12332.
(17) Manthey, J.; Hager, L. P. *Biochemistry* **1989**, *28*, 3052–3057.
(18) Manthey, J.; Hager, L. P. *J. Biol. Chem.* **1981**, *256*, 11232–11238; **1985**, *260*, 9654–9659.
(19) Kanofsky, J. R. *Arch. Biochem. Biophys.* **1989**, *274*, 229–234.
(20) Yiin, B. S.; Margerum, D. W. *Inorg. Chem.* **1990**, *29*, 2135–2141.
(21) Zgliczynski, J. M.; Stelmaszynska, T.; Domanski, J.; Ostrowski, W. *Biochem. Biophys. Acta* **1971**, *235*, 419–424.

Articles

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"Pressure-Testing" Marcus–Hush Theories of Outer-Sphere Electron-Transfer Kinetics

Thomas W. Swaddle

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Predictions of the effect of pressure *P* on rate constants *k* of outer-sphere electron-transfer reactions in solution have been made on the basis of Marcus–Hush theory, with adjustments for medium compression, ion pairing, dielectric saturation, solvent electrostriction, nonadiabaticity, and solvent dynamics. A method of estimating the pressure dependence of the solvent refractive index, required by the theory, is given. For solvents of very low dielectric constant *D*, such as chloroform, the calculations are unrealistic because of large opposing Coulombic and Debye–Hückel contributions, as well as extensive ion pairing. For more polar solvents, the theoretical volumes ΔV^* and compressibilities $\Delta\beta^*$ of activation vary strongly and non-linearly with *P*, especially for nonaqueous solvents at low *P*, so that comparison with corresponding experimental quantities cannot be made, except perhaps approximately at the midpoint of the pressure range. Instead, comparisons are made between theoretical and experimental plots of ln (k/k_0) vs *P* ($k = k_0$ at $P = 0$) for 14 self-exchange reactions of metal complexes in aqueous and nonaqueous solvents. The correlations are good for water (except that nonadiabaticity is indicated for $Co(en)_3^{3+/2+}$ and possibility $MnO_4^{2-/-}$), good to poor for polar organic solvents, and unrealistic for solvents of very low *D*. In no case could behavior expected for rate control by solvent dynamics be found.

Introduction

In recent years, several experimental studies of the effects of pressure *P* on the rate constants *k* of symmetrical outer-sphere electron-transfer (self-exchange) reactions of metal complexes ML_x^{z+} and $ML_x^{(z+1)+}$ in various solvents have been reported together with attempts to rationalize the results in terms of adaptations of the Marcus–Hush theory.[1-12] These rationalizations have suffered in some cases from the lack of the necessary physical data for some of the nonaqueous solvents, notably the pressure

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(1) (a) Stranks, D. R. *Pure Appl. Chem.* **1974**, *38*, 303. (b) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966, 979; **1957**, *26*, 867; *Discuss. Faraday Soc.* **1960**, *29*, 21; *Faraday Discuss. Chem. Soc.* **1982**, *74*, 7. (c) Hush, N. S. *Trans. Faraday Soc.* **1961**, *57*, 557.

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dependence of the factor $(n^{-2} - D^{-1})$ where n is the refractive index and D is the dielectric constant (relative permittivity) of the solvent.[1-10] More generally, a piecemeal approach to the calculation of the predicted pressure effects on k (usually expressed in terms of the volume of activation $\Delta V^* = -RT(\partial \ln k/\partial P)_T$) for particular reactions has tended to obscure some of the problems and limitations inherent in the theoretical analysis. One of these problems is that theory indicates (and, in some instances, experiment appears to confirm) that ΔV^* values should themselves be significantly pressure dependent, i.e., that plots of ln k vs P should be nonlinear, so that it is not obvious how theory and experiment might be meaningfully compared.[4-8,11]

In this article, the properties of theoretical models of pressure effects on k are examined systematically, and the problem of making appropriate comparisons of the theoretical and experimental results is considered in the light of the high-pressure kinetic measurements now available.[1-12] This amounts to testing the applicability of the Marcus–Hush theory[1b,c] by assessing its ability to predict the pressure dependence of k. The theory generally does not predict the *absolute* value of k more accurately than to within a factor (usually an overestimate) of about 30–1000,[13-16] but the pressure effect can be expressed in terms of k *relative* to the zero-pressure value k_0, so that one may reasonably hope for cancelation of some of the sources of error in predicted values of k. In addition, we examine means of obtaining approximate values of the pressure dependence of n of solvents for which direct measurements are lacking and use these values in attempts to rationalize kinetic pressure effects for some self-exchange reactions not previously interpreted.[8,9]

Table I. Calculated and Interpolated Experimental Refractive Indices at Elevated Pressures

		refractive index n^a		$(\partial n^{-2}/\partial P)_T/$ 10^{-10} Pa^{-1}	
solvent	P/MPa	eqs 2–5	expt^b	eqs 2–5	expt^b
methanol^c	0	1.3299	1.3299	−3.19	−3.34
	100	1.3582	1.3588	−1.77	−1.77
	200	1.3771	1.3774	−1.25	−1.22
chloroform^d	0	1.4447	1.4447	−3.35	−3.20
	100	1.4834	1.4807	−1.89	−1.72
	200	1.5099	1.5043	−1.34	−1.19

^{a} At 546 nm. ^{b} Calculated from data of Vedam.[18-20] ^{c} 20 °C. ^{d} 25 °C.

Pressure Dependence of Solvent Properties

Reliable measurements of the pressure dependence of n in the 0–200 MPa regime (the range used in almost all electron-transfer studies reported to date) are available for water[17] and a few nonaqueous liquids,[18-20] but are lacking for some important solvents such as acetonitrile and acetone. This is not surprising in view of the considerable technical difficulties involved in making measurements of the accuracy required, and it is more practical to seek instead a general formula based on readily accessible ambient-pressure parameters that can be shown to reproduce n as a function of P with acceptable accuracy for benchmark cases. Most of the formulas considered by Vedam[18-20] are, in effect, interpolation functions that require high-pressure measurements of n to determine one or more parameters. Wherland and coworkers[5] have used the Eykman formula[21]

$$(n^2 - 1)/(n + 0.4)\rho = \text{constant} \qquad (1)$$

where ρ is the density of the liquid, which in some cases[18,22] outperforms such likely alternatives as the Lorenz–Lorentz (Clausius–Mosotti) expression

$$(n^2 - 1)/(n^2 + 2)\rho = Q \qquad (2)$$

in which Q is a constant. Equation 1 is, however, purely empirical, and Eykman's original work[21] involved no high-pressure measurements. Equation 2 has a well-recognized theoretical basis,[23] and Q has been found to be nearly independent of temperature and pressure for a wide variety of fluids[18] from liquid or gaseous hydrogen[24] to water[25] —indeed, Grigull et al.[17] used an equation of this type to interpolate their precise n values for water at various pressures, temperatures, and light wavelengths.

For most liquids, the Tait-type equation

$$1 - (\rho_0/\rho) = c \ln [1 + (P/b)] \qquad (3)$$

may be used to calculate the density and isothermal compressibility $\beta = \rho^{-1}(\partial\rho/\partial P)_T$ by using values of b and c from the literature,[26] and Q may be evaluated from the ambient ("zero") pressure values ρ_0 and n_0 to obtain estimates of n and $(\partial n^{-2}/\partial P)_T$ at elevated pressures. As noted elsewhere (for water),[11] $(\partial n^{-2}/\partial P)_T$ is not significantly dependent upon the choice of wavelength.

$$n = [(1 + 2\rho Q)/(1 - \rho Q)]^{1/2} \qquad (4)$$

$$(\partial n^{-2}/\partial P)_T = -3Q\rho\beta/(2\rho Q + 1)^2 \qquad (5)$$

An exception to the applicability of this procedure is water below about 30 °C, for which eq 3 represents the density data very poorly (cf. the anomalous maximum in ρ_0 at 4 °C). In this case, Grigull's polynomial interpolation[27] of the density data should be used. In general, eq 3–5 give values of $(\partial n^{-2}/\partial P)_T$, which may be up to about 10% too negative (cf. Chen and Vedam[20]) but are, for the most part, close enough to the experimental values to be acceptable for the present purposes. Table I shows a "good" (methanol) and a "bad" (chloroform) example.

The pressure dependence of D has been determined experimentally for most chemically important nonaqueous solvents[28]

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(2) Swaddle, T. W. In *Inorganic High Pressure Chemistry: Kinetics and Mechanism*; van Eldik, R., Ed.; Elsevier: Amsterdam, 1986; Chapter 5.

(3) Spiccia, L.; Swaddle, T. W. *Physica B+C (Amsterdam)* **1986**, *139/140B+C*, 684.

(4) Spiccia, L.; Swaddle, T. W. *J. Chem. Soc., Chem. Commun.* **1985**, 67; *Inorg. Chem.* **1987**, *26*, 2265; **1988**, *27*, 4080.

(5) Nielson, R. M.; Hunt, J. P.; Dodgen, H. W.; Wherland, S. *Inorg. Chem.* **1986**, *25*, 1964.

(6) Doine, H.; Swaddle, T. W. *Inorg. Chem.* **1988**, *27*, 665.

(7) Stebler, M.; Nielson, R. M.; Siems, W. F.; Hunt, J. P.; Dodgen, H. W.; Wherland, S. *Inorg. Chem.* **1988**, *27*, 2893.

(8) Doine, H.; Swaddle, T. W. *Can. J. Chem.* **1988**, *66*, 2763.

(9) Doine, H.; Yano, Y.; Swaddle, T. W. *Inorg. Chem.* **1989**, *28*, 2319.

(10) Kirchner, K.; Dang, S.-Q.; Stebler, M.; Dodgen, H.; Wherland, S.; Hunt, J. P. *Inorg. Chem.* **1989**, *28*, 3604.

(11) Jolley, W. H.; Stranks, D. R.; Swaddle, T. W. *Inorg. Chem.* **1990**, *29*, 385.

(12) Jolley, W. H.; Stranks, D. R.; Swaddle, T. W. *Inorg. Chem.* **1990**, *29*, 1948.

(13) Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 5615.

(14) Brunschwig, B. S.; Creutz, C.; Macartney, D. H.; Sham, T.-K.; Sutin, N. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 113.

(15) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.

(16) Sutin, N.; Brunschwig, B. S.; Creutz, C.; Winkler, J. R. *Pure Appl. Chem.* **1988**, *60*, 1817.

(17) Thormählen, I.; Straub, J.; Grigull, U. *J. Phys. Chem. Ref. Data* **1985**, *14*, 933.

(18) Vedam, K. *Crit. Rev. Solid State Mater. Sci.* **1983**, *11*, 1.

(19) Vedam, K.; Limsuwan, P. *J. Chem. Phys.* **1978**, *69*, 4762, 4772; *J. Appl. Phys.* **1979**, *50*, 1328.

(20) Vedam, K.; Chen, C. C. *J. Chem. Phys.* **1982**, *77*, 1461.

(21) Eykman, J. F. *Recl. Trav. Chim. Pays-Bas* **1895**, *14*, 201. Eykman's equation is misprinted in ref. 5.

(22) Gibson, R. E.; Kincaid, J. F. *J. Am. Chem. Soc.* **1938**, *60*, 511.

(23) Raman, V.; Venkataraman, K. S. *Proc. R. Soc. London, A*, **1939**, *171*, 137.

(24) Diller, D. E. *J. Chem. Phys.* **1968**, *49*, 3096.

(25) Eisenberg, H. *J. Chem. Phys.* **1965**, *43*, 3887.

(26) Isaacs, N. S. *Liquid Phase High Pressure Chemistry*; Wiley: New York, 1981; p 71. Note that Isaacs' C values should be divided by ln 10 to give c.

(27) Grigull, U., Ed. *Properties of Water and Steam in SI Units*; Springer: Berlin, 1982.

(28) Reference 26, p 99 (for logarithms to base 10; note also that Isaacs' function Φ is negative).

Table II. Parameters for Eqs 3–6

solvent	$T/°C$	b/MPa	c	ρ_0/kg m^{-3}	b'/MPa	$c'/10^{-3}$	D_0	n_0[a]
CH_3CN	25	92.52	0.1029	776.0	126.0	3.75	36.1	1.3417
	0	104.4	0.1008	801.1	169.3	3.40	40.85	1.3540
$(CH_3)_2CO$	25	81.5	0.1023	785.5	66.4	5.13	20.75	1.3568
CH_3OH	25	84.6	0.0977	786.7	100.4	3.67	32.73	1.3277
	0	116.6	0.1050	811.4	134.6	3.32	37.98	1.3391
	−40	124.1	0.0948	846.9	166.	2.63	48.91	1.3555
CH_2Cl_2	25	102.8	0.1025	1345.2	62.8[b]	10.81[b]	8.64[b]	1.4215
$CHCl_3$	25	105.2	0.1038	1479.4	80.3	20.51	4.72	1.4426

[a] At 589 nm. [b] At 30 °C.

including acetonitrile[29,30] and can be represented satisfactorily by eq 6.

$$1 - (D_0/D_P) = c'D_0 \ln [1 + (P/b')] \qquad (6)$$

This is obviously related to eq 3, implying that the pressure dependences of both n and D are, to a good approximation, simply functions of the solvent density. As noted below, Marcus–Hush theory implies that pressure effects on k will be dominated by terms involving the solvent properties n, D, ρ, and β. Insofar as the theory is correct, then, this means that, *for simple adiabatic outer-sphere electron-transfer reactions in general, the pressure effect on the rate constant is governed almost entirely by solvent density and compressibility*, in the absence of complications such as rate control by solvent dynamics.

Constants for eqs 3–6 for some nonaqueous solvents considered below are given in Table II. Where necessary, these have been calculated by least-squares regression of literature values[18–20,26,29–35] with some minor interpolations.

Theoretical Approach

General Formalism. Sutin and coworkers[15,16] have presented improved versions of the Marcus–Hush theories[1b,c] of adiabatic electron-transfer rates that may be reduced for our purposes to eqs 7–14 (in SI units).

$$k = 4000\pi N\sigma^2\kappa_{el}\nu_n\delta\sigma \exp(-\Delta G^*/RT) \qquad (7)$$

$$\delta\sigma \simeq \sigma/3 \qquad (8)$$

$$\Delta G^* = \Delta G_{IR}^* + \Delta G_{SR}^* + \Delta G_{COUL}^* + \Delta G_{DH}^* \qquad (9)$$

$$\Delta G_{SR}^* = (Ne/16\pi\epsilon_0)[(1/2r_1) + (1/2r_2) - (1/\sigma)](n^{-2} - D^{-1}) \qquad (10)$$

$$\Delta G_{COUL}^* = [Nz(z+1)e^2/4\pi\epsilon_0]/D\sigma \qquad (11)$$

$$\Delta G_{DH}^* = -2RTz(z+1)CI^{1/2}/(1 + BaI^{1/2}) \qquad (12)$$

$$B = e(2N\rho/\epsilon_0 Dk_BT)^{1/2} \qquad (13)$$

$$C = (2\pi N\rho)^{1/2}(e^2/4\pi\epsilon_0 Dk_BT)^{3/2} \qquad (14)$$

Here, σ is the M–M separation associated with the maximum probability of electron transfer; κ_{el} is the electronic transmission coefficient (=1 for adiabatic electron transfer, ≪1 for nonadiabatic transfer—see below); ν_n is the nuclear frequency (assumed to be pressure-independent for the present purposes); r_1 and r_2 are the radii of the envelopes of the first coordination spheres of ML_x^{z+} and $ML_x^{(z+1)+}$ respectively; a, B, and C are the Debye–Hückel parameters; ρ is the density of the solvent; the subscripts IR, SR, COUL, and DH refer to the contributions to the free energy of activation ΔG^* from internal (ligand) reorganization, solvent reorganization, the Coulombic work of bringing the reactants together, and the effect of ionic strength I (Debye–Hückel), respectively; and the other symbols have their usual meanings. In the predominant current view,[15] electron transfer occurs at an appreciable rate over a *range* $\delta\sigma$ of M–M separations, rather than wholly at a unique distance σ. Thus, σ is identified as the separation at which electron transfer is most probable and is regarded here as a pressure-sensitive variable. We will follow precedent[15] in correlating $\delta\sigma$ with σ as in eq 8.

Through most of the following discussion, σ_0, the value of the M–M separation σ at zero pressure, is arbitrarily set to $(r_1 + r_2)$; i.e., electron transfer is taken to be most probable at contact of the first coordination sphere envelopes. Nevertheless, σ will still be pressure dependent, since r_1 and r_2 are not well-defined and interpenetration of the ligands is expected to occur.[12,36] A rigorous calculation of the pressure dependence of σ would involve detailed consideration of all the short-range intermolecular interactions present in the precursor assemblage, and this is clearly impractical. If, however, the precursor assemblage is regarded as being loosely confined within a cavity in the solvent, intermolecular distances inside the cavity, specifically the M–M separation, may be taken to compress approximately as does the medium, so that σ will be proportional to $\rho^{-1/3}$. This approximation probably overestimates the pressure effect on σ, but should be more realistic (and tractable) than an assumption at the lower extreme of compressibility, viz., that the precursor assemblage compresses as would a solid of comparable composition. It will shown below that the choice of σ_0 does not exert a major influence on the calculated effect of pressure on k.

Equation 10 is not strictly valid for $\sigma < (r_1 + r_2)$,[16] but as far as prediction of pressure effects is concerned, it may be assumed to hold with adequate precision for small degrees of interpenetration of the first coordination spheres. Kharkats[37] has pointed out that eq 10 should in any event be modified to allow for the "cutout" effect of the proper volumes of the ions and the larger but opposing effect of field distortion, but these adjustments produce only small corrections to the predicted effects of pressure (<1 cm^3 mol^{-1} in ΔV^*) in typical cases,[4] and eq 10 has therefore been used as such in the calculations discussed below.

As noted in the Introduction, it has been customary in the field of high-pressure kinetics to express the pressure dependence of reaction rates in terms of a volume of activation ΔV^*; if the ln k vs P plot is curved, a "compressibility coefficient of activation" $\Delta\beta^* = -(\partial\Delta V^*/\partial P)_T$ is usually introduced. Thus, Stranks[1a] and others[2–10] have used eq 15 and other pressure derivatives of eq 9–14 to calculate theoretical volumes of activation for outer-sphere electron transfer.

$$\Delta V^* = \Delta V_{IR}^* + \Delta V_{SR}^* + \Delta V_{COUL}^* + \Delta V_{DH}^* \qquad (15)$$

This procedure is informative in that it reveals that ΔV_{COUL}^* and ΔV_{DH}^* are opposite in sign and tend to cancel (unless D is very low).[1a,2] Furthermore, ΔV_{IR}^* is small enough (usually between 0 and +1 cm^3 mol^{-1})[1a] to be neglected, unless one or both of the reactants is present as a mixture of spin isomers (see discussion of $Co(en)_3^{3+/2+}$, below) or is not rigid (i.e., has flexible ligands that "crumple" under pressure). Thus, the solvent reorganization term ΔV_{SR}^* emerges as the most important component of ΔV^*.[2] The calculations presented below, however, predict that ΔV^* and $\Delta\beta^*$ should be markedly dependent on

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(29) Würflinger, A. *Ber. Bunsen-Ges. Phys. Chem.* **1980**, *84*, 653.
(30) Srinivasan, K. R.; Kay, R. L. *J. Solution Chem.* **1977**, *6*, 357.
(31) Ledwig, R.; Würflinger, A. *Z. Phys. Chem. (Frankfurt)* **1982**, *132*, 21.
(32) Landau, R.; Würflinger, A. *Ber. Bunsen-Ges. Phys. Chem.* **1980**, *84*, 895.
(33) Landolt-Börnstein *Zahlenwerte und Funktionen*; Springer: Berlin, 1971; Vol. 2, parts 1 and 8.
(34) Newitt, D. M.; Weale, K. E. *J. Chem. Soc.* **1951**, 3092.
(35) Hartmann, H.; Neumann, A.; Rinck, G. *Z. Phys. Chem. (Frankfurt)* **1965**, *44*, 204.
(36) Tembe, B. L.; Friedman, H. L.; Newton, M. *J. Chem. Phys.* **1982**, *76*, 1490.
(37) Kharkats, Yu. I. *Sov. Electrochem. (Engl. Transl.)* **1976**, *12*, 566.

pressure over the range (0–200 MPa) commonly used and that their variability should be especially severe at the lowest pressures. It can therefore be very misleading to attempt to compare experimental data, expressed as a single ΔV^* value or as a combination of a ΔV^* with a $\Delta\beta^*$ value, with ΔV^* computed for some particular pressure (usually atmospheric) for which the pressure derivatives of n, D, and ρ are known.

A more realistic way of comparing theory and experiment is simply to plot calculated and measured *relative* ln k values ln (k/k_0), where k_0 is the value of k at zero (in effect, atmospheric) pressure, together against P, as is done below. Usually, k_0 is measurable with relatively high accuracy, while use of k/k_0 rather than k eliminates several sources of theoretical error. The procedure requires that n, D, and ρ be expressible as continuous functions of pressure, as discussed above (eq 1–6 or, for water, the equations of Grigull et al.[17,27]). Theoretical values of ΔV^* can be obtained by computing the change in ln k over very small increments of pressure, and $\Delta\beta^*$ values can be predicted in a similar way.[11,12]

Counterion Effects. Debye–Hückel effects apart, the counterion can affect the rate of outer-sphere electron transfer in two ways: (a) accelerating it by providing a more effective parallel reaction path involving the counterion in the transition state (e.g., alkali-metal catalysis of the $MnO_4^{-/2-}$ exchange[4]) and (b) retarding it by decreasing the reactant pool through the formation of relatively inactive ion pairs.[5-7,38] Phenomenon a is more commonly encountered in electron transfer between anions[4,39] than between cations,[40] while phenomenon b becomes marked in nonaqueous solvents of low D.[5-7] In the examples discussed below, except where otherwise indicated, approximate corrections for the ion pairing effect (b) are made through use of the Fuoss equation[41] as described elsewhere.[11,12] These adjustments are probably overcorrections, inasmuch as Wherland and co-workers[5,7] generally have found that ion pairs are typically about 4 times less reactive than the free ions, rather than totally inactive, but unless ion pairing is strongly dominant, it is better to include the modest corrections calculated for inactive ion pairs than to ignore the effect. The computations include reiterative adjustments (to 0.1% consistency) of the ionic strength I to allow for ion pairing, which is in turn affected by I.

Nonadiabaticity. At separations σ greater than some critical distance d, M–M electronic coupling will become too weak to permit adiabatic electron transfer, i.e., κ_{el} will become less than 1 and will decrease with increasing σ in a manner that is conveniently described by eqs 16 and 17,[8,15,16] where H_{AB} is the

$$\kappa_{el}\nu_n = (H_{AB}{}^2/h)(\pi^3/RT\Delta G^*)^{1/2} \qquad (16)$$

$$H_{AB}{}^2 = (H_{AB}{}^0)^2 \exp[-2\alpha(\sigma - d)] \qquad (17)$$

electronic coupling matrix element and α is a distance scaling factor, which can be estimated theoretically or obtained indirectly from experimental data in some cases and is typically 6–25 nm^{-1}.[15,16] The transition between adiabatic and nonadiabatic behavior will obviously not be abrupt as is implied by eq 17,[42] but at least where electron transfer is markedly nonadiabatic there should be a strong dependence of k upon σ and hence, at variable pressure, upon $\rho^{-1/3}$.[11,12] This pressure dependence will derive mainly from the exponential part of eq 17; the change in $\Delta G^{*-1/2}$ (eq 16) with pressure, though included in the following calculations, is relatively small and was justifiably neglected in previous papers,[2-4,11,12] while $H_{AB}{}^0$ can be taken to be pressure independent.

Dielectric Saturation and Related Effects. It is generally conceded that a major weakness in the application of eqs 7–14, and indeed the entire traditional approach to representing the properties of ions in solution, is the assumption that the solvent can be treated as a continuous, structureless dielectric with a uniform relative permittivity D identical with the bulk value. This model is probably quite adequate in cases where the ions are large and of low charge and the solvent molecules are small. Where the reactants are not very much larger than the solvent molecules, such as $MnO_4^{-/2-}$ in water, the two-sphere dielectric continuum model might be supplanted with one in which the reactant ions are considered to occupy an ellipsoidal cavity in the solvent.[2-4] Alternatively, one might introduce some means of representing the saturation of the dielectric in the vicinity of an ion. We have explored the implications for electron-transfer reactions of Abe's suggestion[43] that D_r, the relative permittivity at a distance r from the center of an ion of radius r_{ion}, might be taken to fall exponentially from its bulk value D to 1 at $r = r_{ion}$.

$$D_r = D \exp(-r_{ion}(\ln D)/r) \qquad (18)$$

The value of D at r_{ion}, however, might be better equated with the optical dielectric constant, which we approximate to n^2, and this gives eq 19.

$$D_r = D \exp[(2 \ln n - \ln D)r_{ion}/r] \qquad (19)$$

For electron transfer between $ML_x{}^{z+}$ and $ML_x{}^{(z+1)+}$, r may be arbitrarily set equal to the M–M separation σ. In practice, this "correction" for dielectric saturation has a significant impact on the predicted effects of pressure on k only for small ions of high charge or when D is very low—but in the latter case the calculations are unstable in other respects. The correction is therefore applied below only in a few illustrative examples.

A further effect of ions upon solvent properties is the electrostrictive pressure P_{el}, which they exert simply by virtue of their charge. Following Whalley,[44] we represent this as

$$P_{el} = (D - 1)z^2e^2/32\pi^2\epsilon_0 D^2 r^4 \qquad (20)$$

P_{el} causes D (as well as n and ρ) to *increase* in the vicinity of an ion, so that dielectric saturation is partially offset, and this may account in part for the surprising success of continuous dielectric models in treating properties of ionic solutes. The effect of P_{el} at ranges on the order of σ on electron-transfer rate predictions, however, is quite small and is included here only when eq 19 is invoked.

Solvent Dynamics. The possible influence of solvent dynamics ("friction") on k[45-51] and its response to pressure[8] need be considered only for reactions with very small $\Delta G_{IR}{}^*$. When, in such cases, the solvent relaxes slowly, the contribution ν_s from the solvent to the nuclear frequency factor in eq 7 may become more important than that from the reactants. Following Grampp et al.,[45] we may write

$$\nu_s = \tau_L{}^{-1}(\Delta G_{SR}{}^*/4\pi RT)^{1/2} \qquad (21)$$

in which the solvent longitudinal relaxation time τ_L may be taken to be $\tau_D(D_\infty/D)$, where the limiting high-frequency dielectric constant D_∞ can be approximated to n^2. In the absence of direct measurements of τ_D as a function of P for the solvents of interest, the Debye relaxation time τ_D may be expediently set equal to $3V_M\eta/RT$, where V_M is the molar volume of the solvent and η is its viscosity. Apart from the inherent defects in this approx-

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(38) Gribble, J.; Wherland, S. *Inorg. Chem.* **1989**, *28*, 2859. Borchardt, D.; Wherland, S. *Inorg. Chem.* **1986**, *25*, 901.

(39) Bruhn, H.; Nigam, S.; Holzwarth, J. F. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 129.

(40) Rampi Scandola, A.; Scandola, F.; Indelli, A. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 2967.

(41) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059.

(42) Onuchic, J. N.; Beratan, D. N. *J. Phys. Chem.* **1988**, *92*, 4817.

(43) Abe, T. *J. Phys. Chem.* **1986**, *90*, 713.

(44) Whalley, E. *J. Chem. Phys.* **1968**, *38*, 1400.

(45) Grampp, G.; Harrer, W.; Jaenicke, W. *J. Chem. Soc., Faraday Trans.* **1987**, *83*, 161.

(46) Hynes, J. T. *Annu. Rev. Phys. Chem.* **1987**, *36*, 573.

(47) McManis, G. E.; Golovin, M. N.; Weaver, M. J. *J. Phys. Chem.* **1986**, *90*, 6563.

(48) Nielson, R. M.; McManis, G. E.; Weaver, M. J. *J. Phys. Chem.* **1989**, *93*, 4703.

(49) Frauenfelder, H.; Wolynes, P. G. *Science (Washington, DC)* **1985**, *229*, 337.

(50) Newton, M. D.; Sutin, N. *Annu. Rev. Phys. Chem.* **1984**, *35*, 437.

(51) Rodger, P. M.; Sceats, M. G.; Gilbert, R. G. *J. Chem. Phys.* **1988**, *88*, 6448. Gilbert, R. G. Personal communication.

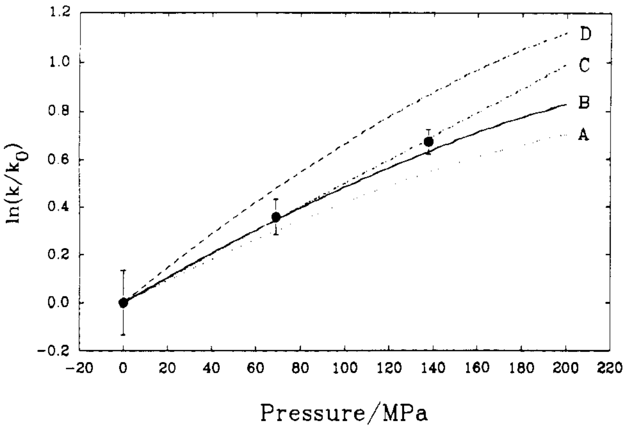

Figure 1. Relative rate constants for the $Fe(H_2O)_6^{3+/2+}$ exchange in aqueous $HClO_4$ (I = 0.5 mol L^{-1}) at 2 °C ($r_1 = r_2$ = 340 pm; a = 620 pm): (A) adiabatic, no ion pairing ($\sigma_0 = r_1 + r_2$); (B) adiabatic with ion pairing (σ = 525 pm); (C) adiabatic as in part B, but with dielectric saturation; (D) nonadiabatic with ion pairing ($\sigma_0 = r_1 + r_2$). Data were taken from ref 12.

imation, the present approach limits consideration of anticipated solvent relaxation phenomena to the aspect of dielectric relaxation, but in the absence of a tractable, comprehensive, statistical-mechanical treatment,[51] it does at least provide a starting point for consideration of how solvent friction might manifest itself in terms of pressure effects.[8] We may write, for ν_s at pressure P relative to zero pressure

$$\nu_s(P)/\nu_s(0) = (DV_M{}^0\eta_0 n_0{}^2/D_0V_M\eta n^2)\ (\Delta G_{SR}{}^{*P}/\Delta G_{SR}{}^{*0})^{1/2} \tag{22}$$

whence the pressure effect on ln (k/k_0), calculated from eq 7–14, may be modified according to eq 23.

$$\ln\ (k/k_0)_{\text{friction}} = \ln\ (k/k_0)_{\text{calc}} + \ln\ (D\rho\eta_0/D_0\rho_0\eta) + [(\ln\ (\Delta G_{SR}{}^{*P}/\Delta G_{SR}{}^{*0}))/2] - 2\ \ln\ (n/n_0) \tag{23}$$

Comparison of Predictions with Experimental Data

The $Fe(H_2O)_6^{3+/2+}$ Exchange in Aqueous Acidic Solution. As noted elsewhere,[12] the pressure effects on the $Fe(H_2O)_6^{3+/2+}$ exchange in aqueous $HClO_4$ can be very satisfactorily accounted for on the basis of essentially adiabatic electron transfer, although it is possible that the maximum electron-transfer probability corresponds to some interpenetration of the ligands ($\sigma_0 \simeq$ 525 pm rather than $\sigma_0 = r_1 + r_2$ = 680 pm) as suggested by Newton and co-workers.[52–54] The implications of a further suggestion by Newton,[55] that charge transfer may be better described as hole transfer rather than electron transfer in this reaction, are not considered in detail here, since the two mechanisms are likely to have similar pressure responses.

Thus, in Figure 1, curve B, which represents fully adiabatic electron transfer with interpenetration to 525 pm and allowance for ion pairing, accounts for the experimental data to within the experimental uncertainty, although curve A shows that reasonable agreement is still obtained if one assumes $\sigma_0 = r_1 + r_2$ and omits the ion-pairing correction. Inclusion of an allowance for dielectric saturation according to eqs 18–20 (curve C) gives a close fit to the data and also removes the curvature seen in curves A, B, and D, but these are largely fortuitous consequences of the anomalous properties of water at low temperatures, since for other solvents as well as for water at higher temperatures eqs 18–20 lead to increased curvature of the ln (k/k_0) vs pressure plots and poorer fits of the data. In practice, the contribution of eqs 18–20 to the overall pressure effect is small unless D is very low, in which case the calculations become grossly unrealistic in any case (see below).

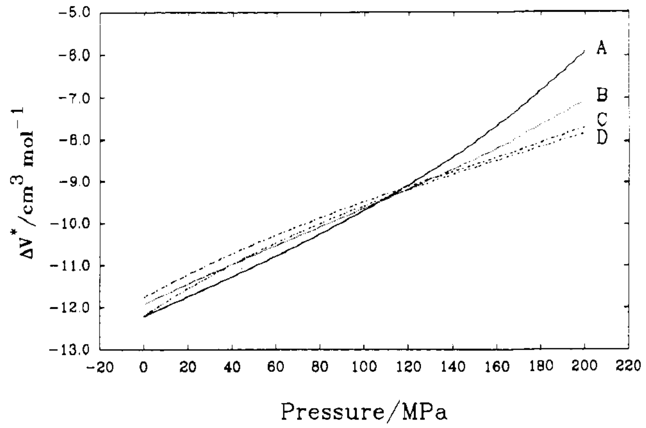

Figure 2. Theoretical volumes of activation for the adiabatic $Fe(H_2O)_6^{3+/2+}$ exchange in aqueous $HClO_4$ (I = 0.5 mol L^{-1}) at temperatures of (A) 2, (B) 10, (C) 25 and (D) 50 °C. $r_1 = r_2$ = 340 pm, a = 620 pm, and σ_0 = 525 pm.

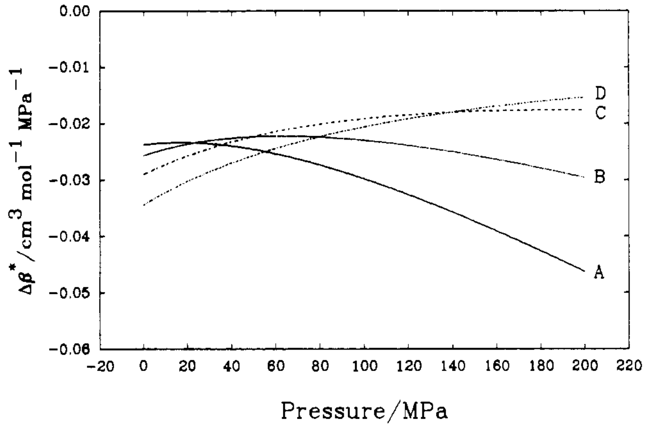

Figure 3. Theoretical compressibility coefficients of activation for the $Fe(H_2O)_6^{3+/2+}$ exchange in aqueous $HClO_4$ with conditions and symbols as in Figure 2.

Curve D in Figure 1 shows that the assumption of nonadiabatic electron transfer with $\alpha \simeq 10\ \text{nm}^{-1}$ [12,50,52–54] at $\sigma \simeq$ 680 nm fails to account for the data to within the experimental uncertainty. It has been pointed out by several authors[56–61] that the hexaaquairon(III/II) self-exchange is some 3 orders of magnitude faster than would be predicted from the rates of net redox reactions (according to the Marcus cross-relation) or of the self-exchange at electrodes. This has been interpreted[56,57] in terms of a ligand-bridged charge transfer in the homogeneous self-exchange reaction, but this mechanism would require a limiting low-pressure $\Delta V_0{}^*$ value near zero,[12] whereas the experimental average value (0–140 MPa) is −11 cm^3 mol^{-1}. Rather, the pressure effects imply that the homogeneous $Fe(H_2O)_6^{3+/2+}$ self-exchange is adiabatic but possibly marginally so, whereas the cross-reactions and electrode processes may well be nonadiabatic.[12,58–61]

The difficulty inherent in attempting to interpret pressure effects on electron-transfer reaction rates in terms of a single volume of activation ΔV^* is epitomized by Figure 2, which shows that ΔV^* depends markedly upon the pressure. As it happens, this variability is especially severe for the experimental temperature (2 °C, plot A), and actually worsens as the pressure increases, as a consequence of the anomalous properties of water in this temperature regime. For 25 °C and above, where water behaves more like a "normal" liquid, the theoretical ΔV^* shows a less pronounced but still strong pressure dependence that is almost independent

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(52) Newton, M. D. In *Mechanistic Aspects of Inorganic Reactions*; Rorabacher, D. D., Endicott, J. F., Eds.; ACS Symposium Series 198; American Chemical Society: Washington, DC, 1982; p 255.

(53) Tembe, B. L.; Friedman, H. L.; Newton, M. *J. Chem. Phys.* **1982**, *76*, 1490.

(54) Logan, J.; Newton, M. *J. Chem. Phys.* **1983**, *78*, 4086.

(55) Newton, M. D. *J. Phys. Chem.* **1988**, *92*, 3049.

(56) Bernhard, P.; Sargeson, A. M. *Inorg. Chem.* **1987**, *26*, 4122.

(57) Hupp, J. T.; Weaver, M. J. *Inorg. Chem.* **1983**, *22*, 2557.

(58) Fürholz, U.; Haim, A. *Inorg. Chem.* **1985**, *24*, 3091.

(59) Brown, G. M.; Krentzien, H. J.; Abe, M.; Taube, H. *Inorg. Chem.* **1979**, *18*, 3374.

(60) Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 5615.

(61) Macartney, D. H.; Sutin, N. *Inorg. Chem.* **1983**, *22*, 3530.

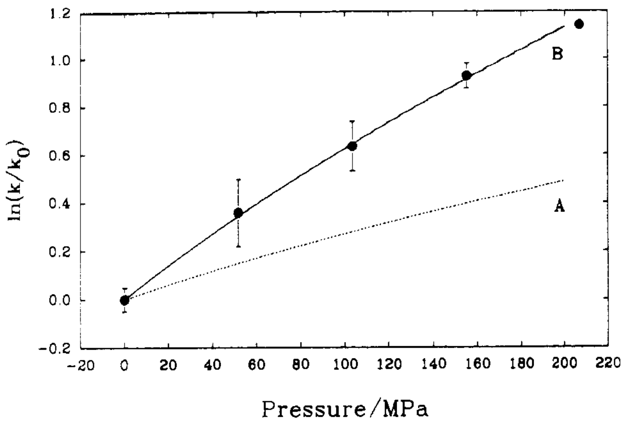

Figure 4. Relative rate constants for the Co(en)$_3^{3+/2+}$ self-exchange in water at 65 °C (I = 0.5 mol L^{-1}; r_1 = 413; r_2 = 398; a = 686; σ_0 = 811 pm). (A) adiabatic electron transfer; (B) nonadiabatic (α = 16 nm^{-1}). Data were taken from ref 11.

of temperature, and this is further illustrated by Figure 3, in which $\Delta\beta^* = -(\partial\Delta V^*/\partial P)_T$ is shown as a function of pressure. Calculations for several nonaqueous solvents (see below) confirm that ΔV^* should in general be markedly pressure dependent but relatively little affected by temperature. Clearly, *unique values of* ΔV^* *and* $\Delta\beta^*$ *that would characterize the pressure dependence of k over any appreciable pressure range cannot be expected to exist,* insofar as Marcus–Hush theory and our adaptation of it are correct.

The Co(en)$_3^{3+/2+}$ Exchange in Water. Wherland[62] has pointed out that Stranks' apparent success[1a] in applying Marcus–Hush theory to explain the marked acceleration of the Co(en)$_3^{3+/2+}$ exchange reaction in water by pressure[11] is invalid because of an error in the sign of the Debye–Hückel term. The correct application of the adiabatic theory gives curve A in Figure 4.

As explained in detail elsewhere,[11] the large discrepancy between curve A and the experimental data is not surprising in view of the fact that the original Co^{II} must go from a high-spin to a low-spin configuration somewhere along the reaction coordinate, and the pressure effects are consistent with either adiabatic electron transfer from a low-spin excited state of the Co^{II} in (unfavorable) equilibrium with the high-spin ground state or nonadiabatic electron transfer from the Co^{II} ground state with prompt multiplicity change. The former explanation is appealing but cannot be tested because the effect of pressure on the high-spin/low-spin preequilibrium is unknown. Studies by Binstead and Beattie[63] on the analogous bis(terpyridine)cobalt(III/II) spin equilibrium suggest a pressure dependence of the right magnitude, but unpublished work by H. Doine in our laboratories has shown that at least two equilibria are involved in the terpyridine case and besides the quartet–doublet transition for Co(en)$_3^{2+}$ can be expected to lie at prohibitively high energy. The simplest explanation is that electron transfer takes place nonadiabatically between ground states; a distance scaling factor α of 16 nm^{-1} represents the data accurately (curve B, Figure 4) and is of the magnitude expected.[15]

The MnO$_4^{-/2-}$ Exchange in Aqueous Alkali. Figure 5 shows that the adiabatic model (curve A) cannot accommodate the large experimental acceleration[3,4] (note scale) by pressure of the cation-independent electron-transfer rate. German and co-workers[65] have argued for nonadiabatic electron transfer with α = 15 nm^{-1}, and this comes reasonably close to accounting for the observed pressure effect (curve B of Figure 5); if, as noted above, the Fe(H$_2$O)$_6^{3+/2+}$ exchange is only marginally adiabatic, then nonadiabaticity in the MnO$_4^{-/2-}$ case is quite feasible.[4] Dielectric saturation allowances (eq 19) have a negligible effect on the calculations, but close agreement between experiment and theory can be obtained by replacing the spheres-in-contact model of the transition state with one in which these unusually small reactants are enclosed in an ellipsoidal cavity in the solvent.[2-4] However, it is undesirable for our present purposes to introduce special models for specific cases, and in any event, the result of the nonadiabatic calculation seems adequate in view of the experimental uncertainties involved in extracting the data of Figure 5 from a two-term rate equation.[3,4]

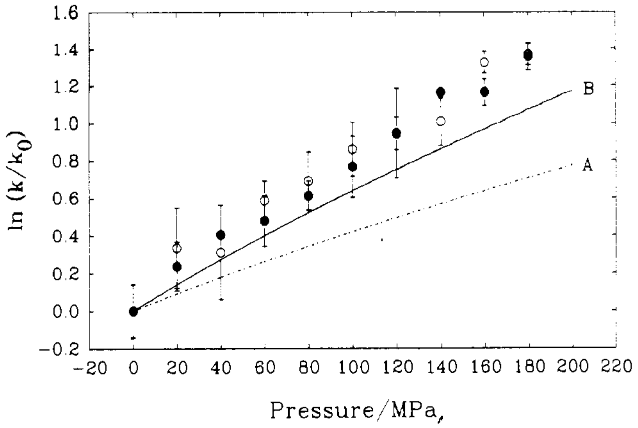

Figure 5. Relative rate constants for the MnO$_4^{-/2-}$ self-exchange in aqueous alkali at 45 °C (I = 1.1 mol L^{-1}; $r_1 = r_2$ = 280 pm; σ_0 = 560 pm): (●) counterion K$^+$ (a = 310 pm); (○) Na$^+$ (a = 360 pm) with values of a taken from ref 64; (A) adiabatic electron transfer. (B) nonadiabatic (α = 15 nm^{-1}). Data were taken from ref 4.

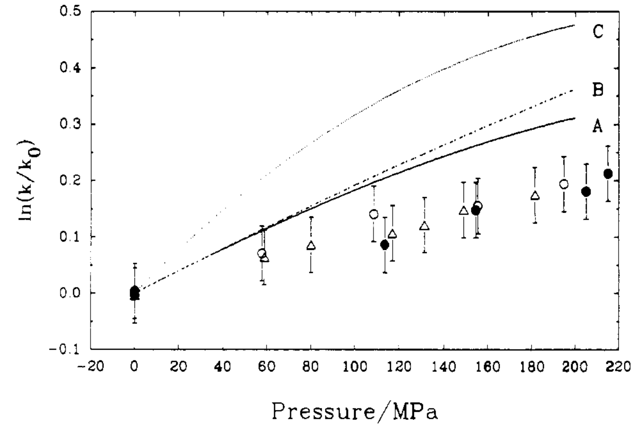

Figure 6. Fe(phen)$_3^{3+/2+}$ in D$_2$SO$_4$/D$_2$O at 3 °C ($r_1 = r_2$ = 700 pm; a = 980 pm; σ_0 = 1.4 nm): (○) [Fe]$_{\text{total}}$ = 0.035, [D$_2$SO$_4$] = 0.10 mol kg^{-1}; (●) [Fe]$_{\text{total}}$ = 0.07, [D$_2$SO$_4$] = 0.135 mol kg^{-1}; (△) [Fe]$_{\text{total}}$ = 0.105, [D$_2$SO$_4$] = 0.10 mol kg^{-1}; (A) adiabatic electron transfer; (B) transfer as in part A, with dielectric saturation; (C) transfer as in part A, with solvent friction. Data were taken from ref. 8.

The Tris(1,10-phenanthroline)iron(III/II) Exchange in Water. The adiabatic model comes close to accounting for the pressure effect on the Fe(phen)$_3^{3+/2+}$ exchange in acidic aqueous solution (curve A of Figure 6; note that the ln (k/k_0) scale is expanded and the experimental data[8] are unusually consistent, so that agreement is better than it appears at first sight). Allowance for dielectric saturation (curve B) fails to improve the agreement.

The Fe(phen)$_3^{3+/2+}$ exchange is of special interest in that the change in the Fe–N bond lengths following redox is negligible, so that ΔG_{IR}^* is very small, and the reaction is fast and possibly subject to rate limitation by solvent dynamics. The experiments[8] had to be carried out near the freezing temperature, to limit decomposition of the highly oxidizing Fe(phen)$_3^{3+}$, and in this temperature regime the viscosity η of water (here, D$_2$O) actually *decreases* as P rises over the first 100 MPa and then begins to increase. One may assume a two-component model for water, in which one component behaves like a normal liquid with the usual direct exponential dependence of η on pressure while the other (presumably with an ice-I_h-like structure that breaks up under pressure) exhibits a *negative* exponential dependence of η

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[62] Wherland, S. *Inorg. Chem.* **1983**, *22*, 2349.

[63] Binstead, R. A.; Beattie, J. K. *Inorg. Chem.* **1986**, *25*, 1481.

[64] Sørensen, T. S.; Sloth, P.; Schrøder, M. *Acta Chem. Scand.* **1984**, *A38*, 735.

[65] Dolin, S. P.; Dogonadze, R. R.; German, E. D. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 648. German, E. D. Personal communication.

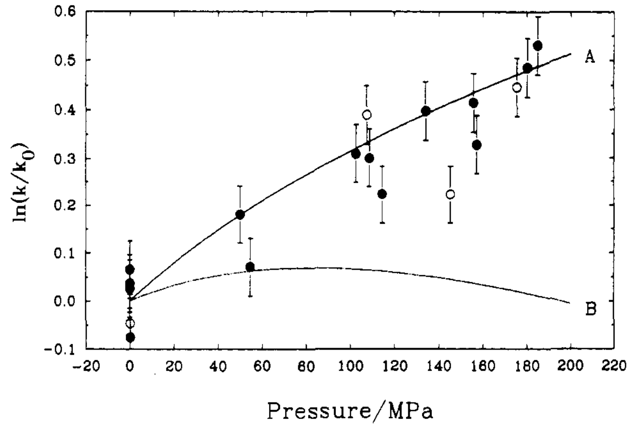

Figure 7. Fe(phen)$_3^{3+/2+}$ in CD_3CN, 4 °C, perchlorate counterion ($r_1 = r_2$ = 700 pm; σ_0 = 1400 pm; a = 980 pm): (●) $[Fe]_{total}$ = 0.067 mol kg^{-1}; (○) $[Fe]_{total}$ = 0.047 mol kg^{-1}. Calculated curves are for 0 °C and I = 0.14 mol kg^{-1} after ion pairing: (A) adiabatic electron transfer. (B) transfer as in part A, with solvent friction. Data were taken from ref 8.

on P. The experimental η values of DeFries and Jonas[66] for D_2O at 3.79 °C, 0.1–600 MPa, may then be represented very well (r^2 = 0.999 982) by a double-exponential equation

$$\eta/10^{-3}\ \text{Pa s} = (A'\exp(B'P)) + (C'\exp(D'P)) \qquad (24)$$

where P is in MPa and A' = 1.0825, B' = −0.005 157, C' = 1.0053 and D' = .00239. Inclusion of eqs 23 and 24 in the calculation of ln (k/k_0) for adiabatic electron transfer gives curve C in Figure 6; clearly, this leads to a worsened fit, which suggests that solvent dynamics do not exert a significant influence on the electron-transfer rate.

The Tris(1,10-phenanthroline)iron(III/II) Exchange in Acetonitrile. Proton NMR line broadening gave less precise rate constants for the Fe(phen)$_3^{3+/2+}$ exchange in CD_3CN than in D_2O,[8] but Figure 7 shows that the adiabatic model (curve A) represents the data for acetonitrile reasonably well in view of the scatter.

Analysis of the data of Salman and Drickamer[67] shows that the viscosity of acetonitrile at 30 °C increases with pressure in the single-exponential manner expected for "normal" liquids (0–300 MPa)

$$\ln \eta = -3.365 + 0.003283P \qquad (25)$$

where η is in Pa s and P is in MPa. The Fe(phen)$_3^{3+/2+}$ exchange in CD_3CN was studied at 3.8 °C,[8] but the *slope* of eq 25 is probably not very different at this temperature (these temperatures are in the middle of the normal liquid range of acetonitrile). Curve B in Figure 7 combines eqs 23 and 25 with the adiabatic model to represent approximately the pressure dependence of ln k with solvent friction; as with water as the solvent, the fit is *worsened* by inclusion of solvent dynamics, although the friction "correction" is now in the *opposite direction* and implies *positive* values for ΔV^* above about 70 MPa, which is certainly at variance with observation. Thus, even if the predictions of eq 23 are only qualitatively correct, it may be concluded that the rate of the Fe(phen)$_3^{3+/2+}$ exchange is not influenced appreciably by solvent dynamics in either CD_3CN or D_2O.

Thus far, then, the Marcus–Hush model (including an adjustment for ion pairing) has proved to be reasonably successful in accounting for pressure effects on outer-sphere self-exchange rates in both water and acetonitrile, if nonadiabaticity effects are allowed for where there are independent reasons for invoking them. This applies whether the exchange is fast or slow.

The Tris(hexafluoroacetylacetonato)ruthenium(III/II) Exchange in Nonaqueous Solvents. In principle, the Ru(hfac)$_3^{0/-}$ exchange provides an ideal test case, since the lack of charge on the Ru^{III} complex means that the Coulombic (work) and Debye–Hückel contributions are negligible, and depletion of the Ru^{II} pool by ion pairing with the counterion should be negligible except in solvents of very low D. The same feature, unfortunately, makes for low solubility of Ru(hfac)$_3^0$ in water, and self-exchange rate measurements were feasible only for nonaqueous media.[6] For CD_3CN as solvent, curve A of Figure 8 embodies the assumptions that the reaction is adiabatic and that both ion pairing and the internal reorganization contribution ΔV_{IR}^* to the pressure effect can be neglected; it predicts a substantially larger pressure acceleration than was found. Any contributions from ion-pair effects (see below) or nonadiabaticity would worsen the discrepancy, while arbitrary inclusion of an unusually large[68] ΔV_{IR}^* of +3 cm^3 mol^{-1} (curve B) neither closes the gap completely nor accounts for the lack of significant curvature in the trend of the experimental ln (k/k_0) values with pressure. Solvent friction is not expected to affect the rate of the Ru(hfac)$_3^{0/-}$ exchange, which is slightly slower than for Fe(phen)$_3^{3+/2+}$ in acetonitrile, and indeed the retrograde curve C fails to match the data even qualitatively above 100 MPa.

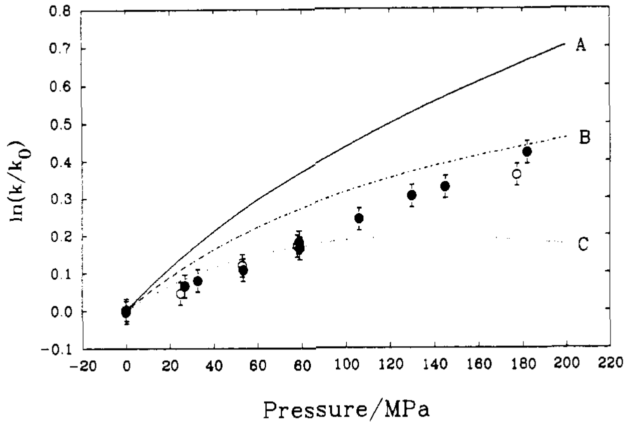

Figure 8. Adiabatic Ru(hfac)$_3^{0/-}$ exchange in CD_3CN at 25 °C: (●) $[Ru]_{total}$ = 0.059 mol kg^{-1}; (○) $[Ru]_{total}$ = 0.033 mol kg^{-1}; (A) ΔV_{IR}^* = 0; (B) ΔV_{IR}^* = 3 cm^3 mol^{-1}; (C) exchange as in part A, but with solvent friction. $r_1 = r_2$ = 500, a = 780, and σ_0 = 1000 pm.

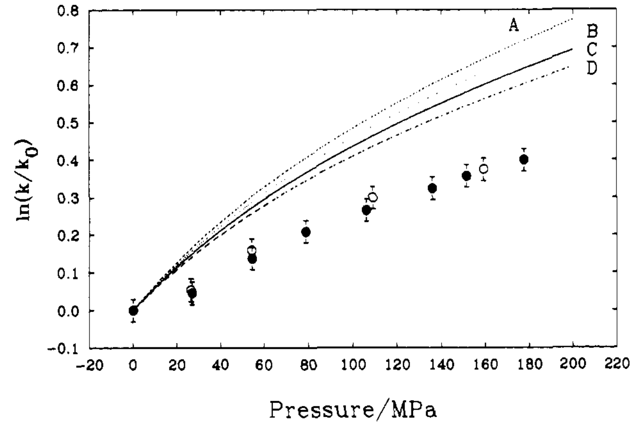

Figure 9. Adiabatic Ru(hfac)$_3^{0/-}$ exchange in CD_3OD at 25 °C: (●) $[Ru]_{total}$ = 0.026 mol kg^{-1}; (○) $[Ru]_{total}$ = 0.060 mol kg^{-1}. $r_1 = r_2$ = 500 pm, and a = 780 pm. Zero-pressure Ru–Ru separation σ_0 is (A) 1600, (B) 1200, (C) 1000, and (D) 800 pm. Calculated curves were for I = 0.05 mol kg^{-1}, ion pairing neglected. Data were taken from ref 6.

The Ru(hfac)$_3^{0/-}$ self-exchange reactions in methanol-d_4 (Figure 9) and acetone-d_6 (Supplementary Figure S1)[6] exhibit the same phenomena as in CD_3CN. In the foregoing calculations, σ_0 has been arbitrarily set at ($r_1 + r_2$); Figure 9 shows that the calculated pressure effects increase with σ_0 but are not very sensitive to this choice, and certainly no physically meaningful value of σ_0 can bring the theoretical curves close to the experimental data in this case.

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(66) DeFries, T.; Jonas, J. *J. Chem. Phys.* **1977**, *66*, 5393.

(67) Salman, O. Ph.D. Thesis, University of Illinois, 1982. Drickamer, H. G. Personal communication.

(68) Calculated values of ΔV_{IR}^* range between 0 and 1 cm^3 mol^{-1},[1a] but for electron transfer between ions with t_{2g}^5 and t_{2g}^6 configurations the change in the metal–ligand bond lengths will be very small and hence ΔV_{IR}^* will be effectively zero.

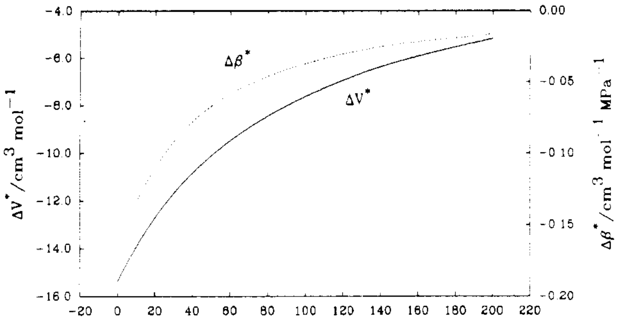

Figure 10. Volume and compressibility coefficient of activation for the $Ru(hfac)_3^{0/-}$ exchange in CD_3OD at 25 °C. Conditions were as for Figure 9, with $\sigma_0 = 1000$ pm.

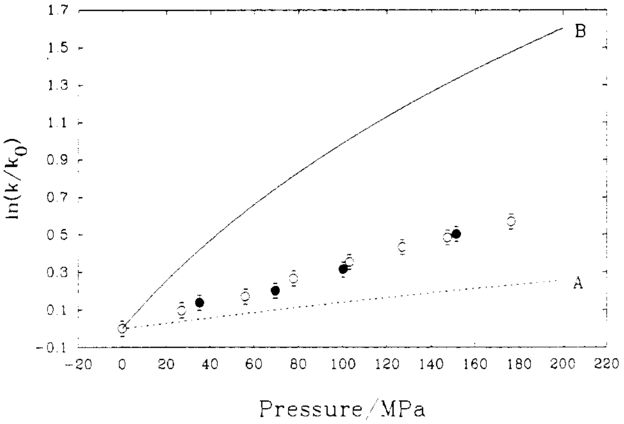

Figure 11. Adiabatic $Ru(hfac)_3^{0/-}$ exchange in $CDCl_3$ at 25 °C: (●) $[Ru]_{total} = 0.0075$ mol kg^{-1}; (○) $[Ru]_{total} = 0.0066$ mol kg^{-1}. (A) no ion pairing; (B) ion pairing allowed for. $r_1 = r_2 = 500$, $a = 780$, and $\sigma_0 = 1000$ pm. Data were taken from ref 6.

Figure 10 shows that, for $Ru(hfac)_3^{0/-}$ self-exchange in methanol, the theoretical values of ΔV^* and, worse still, its negative pressure derivative $\Delta\beta^*$ vary enormously over the experimental pressure range—more so than for the aqueous $Fe(H_2O)_6^{3+/2+}$ case discussed above (Figures 2 and 3). *It is clearly impossible to make any precise connection between theoretical* ΔV^* *values and those obtained by fitting experimental ln k values to a linear function in pressure*—yet linearization is often the best way to represent the experimental data, particularly where they show substantial scatter. Even for those *nonaqueous* solvents for which the experimental data are sufficiently precise to show curvature of the ln k vs P plot of the magnitude predicted (e.g., Figures 6, 8, and 9), this curvature is much less than expected and usually negligible. Thus, plots of ln (k/k_0) vs pressure provide a much more revealing test of theory against experiment than do the ΔV^* values used previously,[1-10] and under such scrutiny theory holds up less well than previously claimed, at least for nonaqueous systems.

For the $Ru(hfac)_3^{0/-}$ self-exchange in $CDCl_3$, the effects of pressure on n^{-2} and D^{-1} almost cancel, and if ion pairing is neglected, the predicted pressure acceleration of ln (k/k_0) becomes very slight (curve A of Figure 11). For solvents of even lower D, theory suggests that electron transfer could be *retarded* by pressure (i.e., ΔV^* could become positive). In practice, however, low D values also lead to depletion of the pool of any charged reactant through ion pairing with the counterions, so there will also be an accelerative contribution from pressure, which favors break-up of ion pairs because it increases D. Indeed, the $Ru(hfac)_3^{0/-}$ self-exchange is an order of magnitude slower in $CDCl_3$ than in more polar solvents, and the observed acceleration by pressure is markedly greater than that predicted by the free-ion model (curve A).[6] However, this acceleration is much less than that calculated with allowance for the formation of unreactive Fuoss ion pairs[11,12,41] and concomitant ionic strength changes (Figure 11, curve B). The overcorrection in curve B probably implies that the ion pairs are not totally inactive in electron transfer but are simply less efficient than the corresponding free ion (cf. Wherland et al.[5,7]). Adjustments for Abe-type dielectric saturation do not affect curve B appreciably. An earlier Marcus–Hush–Fuoss analysis[6] in terms of ΔV^* seemed to be more successful, but factors such as the effect of ion pairing on I were overlooked.

A major problem in attempting to predict relative rates for ion-ion reactions as functions of pressure in solvents of very low D is that the terms ΔV_{COUL}^* and ΔV_{DH}^* in eq 15 become very large (on the order of -50 and $+50$ cm^3 mol^{-1} respectively) and extremely sensitive to D. Thus, although they are of opposite sign, they do not cancel, and the highly imprecise difference between them swamps the calculation even before the ill-defined effects of ion pairing are considered. There appears to be little hope of applying Marcus–Hush theory realistically to the interpretation of pressure effects on electron-transfer rates in media of very low dielectric constant.

The Bis(2,9-dimethyl-1,10-phenanthroline)copper(II/I) Exchange in Nonaqueous Solvents. The pressure dependence of the $Cu(dmp)_2^{2+/+}$ exchange rate in acetone (Supplementary Figure S2) is quite well represented by the adiabatic model, but this overestimates ln (k/k_0) by a factor of about 2 for acetonitrile as solvent (Supplementary Figure S3). This analysis, which was not previously possible because of lack of $(\partial n/\partial P)_T$ data,[9] implies that this exchange reaction is outer sphere and quite "well-behaved" in the Marcus–Hush sense.

The Hexa(organoisonitrile)manganese(II/I) Self-Exchanges in Acetonitrile. Wherland and co-workers have undertaken a very extensive study of the self-exchange kinetics of couples of the type $Mn(CNR)_6^{2+/+}$ in several nonaqueous solvents, often as a function of pressure.[5,7,69] For R = *tert*-butyl in acetonitrile (Supplementary Figure S4), the adiabatic model fits the data well. The experimental measurements were at two different temperatures, but the theoretical ln (k/k_0) values show almost identical pressure dependences at 0 and at 25 °C; in general, theory predicts that ΔV^* should be almost independent of temperature for most outer-sphere electron-transfer systems in most solvents. For R = ethyl in acetonitrile, however, theory overestimates the pressure effect, while for R = cyclohexyl the exchange rates become much faster than predicted above 60 MPa (Supplementary Figures S5 and S6). It should be noted that the last two examples differ from the others considered here in that the ligand systems are nonrigid, and some significant conformational changes leading to altered r_1, r_2, and σ may occur under pressure.

The Ferrocene–Ferrocenium Exchange in Acetonitrile. Hunt, Wherland and co-workers have reported a high-pressure proton NMR study of the very fast $Fe(\eta^5\text{-}C_5H_5)_2^{+/0}$ self-exchange reaction in CD_3CN,[10] for which solvent dynamics might be important.[70] The standard adiabatic model (without allowance for ion pairing, which, like ΔV_{COUL}^* and ΔV_{DH}^*, should be negligible for this system) overestimates the pressure effect in the lower ranges, while the model incorporating solvent dynamics underestimates it seriously above 100 MPa (Supplementary Figure S7). It seems that solvent dynamics are not very important in this system, but may become significant in the cobaltocene/cobaltocenium exchange,[70] which, unfortunately, is too fast for study by high-pressure NMR spectroscopy.

Conclusions

According to the foregoing development of Marcus–Hush theory, the pressure dependence of ln (k/k_0) should be distinctly nonlinear in water and markedly so in nonaqueous solvents such as acetonitrile. Both ΔV^* and $\Delta\beta^*$ are predicted to vary sharply and nonlinearly with pressure, so that there would seem to be dangers in attempting to use Marcus–Hush theory to interpret experimental results expressed in terms of these parameters. On the other hand, the kinetic effects of pressure are predicted to be almost independent of temperature, except in water at low temperatures.

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(69) Nielson, R. M.; Wherland, S. *Inorg. Chem.* **1984**, *23*, 1338; **1986**, *25*, 2437; *J. Am. Chem. Soc.* **1985**, *107*, 1505.

(70) Nielson, R. M.; McManis, G. E.; Safford, L. K.; Weaver, M. J. *J. Phys. Chem.* **1989**, *93*, 2152 and references cited therein.

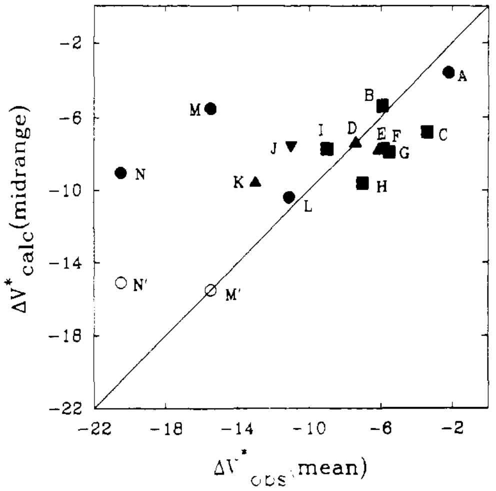

Figure 12. Calculated and observed ΔV^* values at midrange of pressure (100 MPa, except 70 MPa for $Fe(H_2O)_6^{3+/2+}$) for adiabatic (filled symbols) and nonadiabatic (open circles) self-exchange in couples with rigid ligands. Solvents: (○, ●) water; (■) CD_3CN; (▲) $(CD_3)_2CO$; (▼) CD_3OD. Key: (A, B) $Fe(phen)_3^{3+/2+}$; (C, D) $Cu(dmp)_2^{2+/+}$; (E–G) $Ru(hfac)_3^{0/-}$; (H) $Fe(C_5H_5)_2^{+/0}$; (I–K) $Mn(CN\text{-}t\text{-}Bu)_6^{2+/+}$; (L) $Fe(H_2O)_6^{3+/2+}$; (M, M′) $Co(en)_3^{3+/2+}$; (N, N′) $MnO_4^{2-/-}$. Experimental data were taken from refs 4–12. The straight line represents exact agreement between theory and experiment.

Figures 1–11 and Supplementary Figures S1–S7 show that correspondence between calculated ln (k/k_0) vs P plots and the experimental data is good only in a limited number of cases. For nonaqueous solvents in particular, the theoretical plots tend to be too sharply curved at the lower end of the pressure range, although the slopes around the middle of the range and above generally match the trend of the measurements. The discrepancies between theory and experiment cannot be ascribed to inadequacies in the treatment of interactions of highly charged ions with the medium and with other ions, since systems involving a neutral redox partner are among those most poorly described. There is no obvious pattern of successes and failures, and it may be that each couple has special features, such as nonadiabatic behavior or possibilities for interpenetration of the ligands, that would preclude application of any general theory of redox rates.

The comparison of plots of ln (k/k_0) vs P is cumbersome and may be too severe a test of theory; one might wish for a simpler, if less rigorous, criterion of the adequacy of the models. As a compromise, one can calculate ΔV^* from theory for the *midpoint* of the experimental pressure range and compare it with a *mean* ΔV^* value obtained by linearizing the experimental ln k vs P plot (often, this is in any case the only statistically significant way to represent the measurements). This is done in Figure 12 for self-exchange reactions of some rigid complexes in relatively polar solvents—reactions in solvents of low D such as chloroform have been omitted because of the instability of the theoretical calculations. If the aqueous $Co(en)_3^{3+/2+}$ and $MnO_4^{-/2-}$ cases are either excluded or, as justified above, taken as non-adiabatic (points M′ and N′), it can be seen that there is at least *qualitative* agreement between theory and experiment—all the ΔV^* values are negative, those $|\Delta V^*|$ values predicted to be relatively small are indeed small, etc. The number of points falling on or close to the plotted line of exact correspondence, however, is disappointingly small.

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Supplementary Material Available: Plots of ln (k/k_0) vs P for $Ru(hfac)_3^{0/-}$ in acetone, $Cu(dmp)_2^{2+/+}$ in acetone and in acetonitrile, and $Mn(CNR)_6^{2+/+}$ and $Fe(C_5H_5)_2^{+/0}$ in acetonitrile (Supplementary Figures S1–S7) (7 pages). Ordering information is given on any current masthead page.

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Synthesis of Polyhydroxy Carboxylates. 5. Metal Ion Catalyzed O-Alkylation of Ethylene Glycol with Maleate. A Multinuclear NMR Study of the Lanthanide(III) Complexes Present in the Reaction Mixture of the Lanthanide(III)-Catalyzed Reaction

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The structures and stabilities of Ln^{III} complexes occurring in the reaction mixture of a Ln^{III}-catalyzed O-alkylation of ethylene glycol (EG) with maleate (MAL) have been investigated with the use of ^{139}La, ^{17}O, and ^{13}C NMR shift and relaxation measurements and with potentiometry. In EG the Ln^{III} ion appears to be coordinated by nine oxygen atoms; chloride counterions are not present in the first coordination sphere. The Ln^{III} ions have some preference for coordination of EG over that of water. MAL is able to coordinate with the Ln^{III} ions in EG medium. The mono-O-alkylation product of EG (EGMS) forms 1:1 and 1:2 Ln^{III} complexes, in which the ligand is bound in a tetradentate fashion via the two carboxylate groups and the two oxygens of the EG residue. The Ln^{III} coordination of the di-O,O′-alkylation product (EGDS) is analogous; all carboxylate groups and ether oxygens are coordinated.

Introduction

Polyfunctional carboxylates containing an α-(hydr)oxy function are known to be good sequestering agents for metal ions.[1] Recently, we have reported on the synthesis of some compounds of this class by a metal ion catalyzed O-alkylation reaction of di- and polyhydroxy compounds with maleate (MAL).[2] For instance, O-alkylation of ethylene glycol (EG) with MAL, in the presence of multivalent metal cations as catalysts, yields ethylene glycol monosuccinate (EGMS). In a consecutive step, another O-alkylation with MAL can give ethylene glycol disuccinate (EGDS) (see Scheme I). The metal ion probably functions as a template, and it may activate a hydroxyl group of EG and EGMS via ionization upon coordination.

This paper reports on the characterization of metal ion complexes in the reaction mixture of the lanthanide(III)-catalyzed O-alkylation reaction of EG with MAL, using multinuclear NMR

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(1) Smith, R. L. *The Sequestration of Metals*; Chapman and Hall: London, 1959; p 105.

(2) van Westrenen, J.; Roggen, R. M.; Hoefnagel, M. A.; Peters, J. A.; Kieboom, A. P. G.; van Bekkum, H. *Tetrahedron* **1990**, *46*, 5741.

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