though as far as the data go they do parallel the MCD data for HgBr$_2$ as expected.

The absorption spectrum of CH$_3$HgCl did not reveal any well-defined bands below 5.2 μm^{-1}, either in solution or in the vapor phase. This observation is consistent with the blue shift of the lowest energy band compared to that for CH$_3$HgBr predicted for LMCT. A blue shift from the bands of HgCl$_2$, where the lowest energy band is 4.9–5.0 μm^{-1}, is also expected so that the lack of an observed band in the measurement region here is quite reasonable.

Conclusions. The absorption and MCD spectra for bands I and II for HgI$_2$ and for bands I and III for CH$_3$HgI can be interpreted in a self-consistent and satisfactory way by the $I^- \rightarrow$ Hg 6s LMCT model, which includes the effects of I$^-$ spin–orbit coupling. The relative absorption intensity is ascribed to the singlet character in the Σ_u^+ or Σ^+ spin–orbit states, but the explanation of the pseudo $\mathcal{A}$ terms in the MCD spectra requires close-lying Σ_u^+ and Π_u or Σ^+ and Π spin–orbit states. The observed blue shift of the CH$_3$HgI spectra relative to the HgI$_2$ spectra is expected within the model because of the stronger σ-donor strength of the CH$_3^-$ ligand compared to that of I$^-$. The long progressions in the bending vibrations that structure band II for HgI$_2$ and bands I and III for CH$_3$HgI provide a strong indication of bound molecular excited states for the LMCT, which are bent and therefore Franck–Condon-shifted relative to the linear ground states. However, the underlying broadness of each of the LMCT bands also suggests the possibility of a dissociative potential surface crossing that of the bound state in the energy region of the band maximum and beyond.

Although the data are not as extensive and the individual features are not as well-resolved, the spectra for HgBr$_2$ and CH$_3$HgBr follow the LMCT pattern in the iodo complexes, except, as expected, shifted to higher energy. The difference in the MCD spectra, together with the changes in the relative intensities for the LMCT bands for the bromo complexes compared to those for the iodo complexes, is compatible with that expected from the lower excited state spin–orbit interaction from Br$^-$ compared to that from I$^-$. Little detail can be extracted from the spectra of HgCl$_2$ and CH$_3$HgCl because of the LMCT blue shift to the edge of our measurement capability or beyond.

Acknowledgment. Helpful discussions with Dr. C. T. Lin are gratefully acknowledged.

Registry No. HgI$_2$, 7774-29-0; HgBr$_2$, 7789-47-1; HgCl$_2$, 7487-94-7; CH$_3$HgI, 143-36-2; CH$_3$HgBr, 506-83-2; CH$_3$HgCl, 115-09-3.

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Pressure Effects on the Rates of Electron Transfer between Tris(hexafluoroacetylacetonato)ruthenium(II) and -(III) in Different Solvents

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Rate constants k for electron transfer between Ru(hfac)$_3^-$ and Ru(hfac)$_3^0$ in the perdeuteriated solvents acetone, acetonitrile, chloroform, and methanol have been measured as functions of pressure up to 200 MPa by ^{1}H NMR spectroscopy. Development of the Stranks–Hush–Marcus (SHM) theory indicates, and the data for methanol confirm, that ln k is a nonlinear function of pressure, but approximation to linear dependence gives the mean experimental ΔV^* values −6 ((CD$_3$)$_2$CO), −5.5 (CD$_3$CN), −8.1 (CDCl$_3$), and −5.8 cm^3 mol^{-1} (CD$_3$OD). For chloroform and methanol, respectively, ΔH^* = 24.5 and 22 (±3) kJ mol^{-1} and ΔS^* = −28 and −41 J K^{-1} mol^{-1}. Ion pairing with the tetra-*n*-butylammonium counterion appears to dominate the kinetics in chloroform. In the other solvents, the kinetics are consistent with adiabatic SHM theory with predominant contributions from solvent reorganization and a secondary contribution (amounting to some 16 kJ mol^{-1} in ΔG^* but only +1 ± 1 cm^3 mol^{-1} in ΔV^*) from internal reorganization within the Ru complexes. The pressure dependence of the ^{1}H line width and chemical shift of tris(acetylacetonato)chromium(III) in the four solvents is also reported.

Introduction

We report here an extension of our continuing studies of the effects of pressure on electron-transfer (ET) kinetics in solution to cover solvents other than water. As comparison of the gas- and solution-phase rates of intermolecular ET reactions of metallocene–metallocenium couples clearly shows,[1] the kinetics of ET reactions can be markedly influenced by solvent effects,[2] which in turn are sensitive to applied pressure. Stranks[3] attempted to develop the classical Hush[4] (cf. Marcus[2]) ET theory to account for the effect of pressure (expressed as the volume of activation ΔV^*) on outer-sphere ET rates but was less successful than at first appeared because of an error in treating the contribution from medium (Debye–Hückel) effects.[5]

An adaptation of Stranks' approach[6] can, however, account quite accurately for the experimental ΔV^* as well as the enthalpy ΔH^* and entropy ΔS^* of activation for the cation-independent pathway for ET between manganate and permanganate ions in aqueous solution. Unfortunately, we have been unsuccessful in attempts to extend our ^{55}Mn-NMR-based kinetic studies of this reaction to nonaqueous solvents; only aprotic solvents can be considered, and most organic solvents (or impurities in them) tend to reduce one or both of the reactants, and the solubility of salts of the manganate ion in particular is often insufficient for the NMR measurements even in the presence of 18-crown-6.[7]

We have therefore turned our attention to the Ru^{II}(hfac)$_3^-$–Ru^{III}(hfac)$_3^0$ self-exchange reaction (hfac = 1,1,1,5,5,5-hexafluoropentane-2,4-dionate), which has been studied by Chan and Wahl[8] in several perdeuteriated organic solvents by measurement of the effect of small amounts of the Ru^{III} complex upon the ^{1}H and ^{19}F NMR line widths of the diamagnetic Ru^{II} partner. Although this system cannot be studied in water, it offers several advantages. The electrical neutrality of the Ru^{III} complex makes it unnecessary to consider ionic medium effects or the Coulombic work terms involved in bringing the reactants together, and (in contrast to the MnO$_4^-$–MnO$_4^{2-}$ case) there is no detectable reaction pathway involving the counterion of the Ru^{II} complex.[8] The reactant molecules are large, so that a "two-sphere" theoretical model that treats the solvent as a continuous dielectric should suffice (again, in contrast to the case of the small MnO$_4^-$–MnO$_4^{2-}$ ions).[6] Chan and Wahl point out[8] that the contribution of internal rearrangement[2–4,6] of the reactants to the reaction rate is not large, and (more importantly, for our purposes) Stranks[3] showed that

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this contribution is only slightly affected by pressure. The influence of solvent reorganization dynamics (which would be sensitive to pressure through dependence upon the solvent viscosity) will also be negligible for the $Ru(hfac)_3^{0,-}$ exchange in typical solvents, as pointed out by Grampp et al.[9] Finally, although, in the absence of the relevant vibrational force constant data, Chan and Wahl[8] did not apply the Marcus theory to estimate the free energy of internal reorganization of the reactants and hence predict the reaction rate absolutely, they showed that the *relative* rates of the $Ru(hfac)_3^{0,-}$ exchange in seven different solvents conformed well with predictions (the rate in $CDCl_3$, however, was an order of magnitude slower than expected).

Thus, the $Ru(hfac)_3^{0,-}$ self-exchange can be expected to provide a good subject for testing the Stranks–Hush–Marcus[3] (SHM) and related[6] theories of pressure effects on outer-sphere ET reactions in nonaqueous solvents. For our purposes, practical considerations (e.g., the freezing of some solvents such as acetic acid under pressure) limited the choice of media to acetone, acetonitrile, chloroform, and methanol, and a pressurizable probehead was available for ^1H NMR measurements only.

Experimental Section

Materials. Acetone-d_6 (MSD Isotopes, 99.9% D), $CDCl_3$ (Aldrich, 99.8% D), and CD_3OD (MSD Isotopes, 99.6% D) were used without further purification. Acetonitrile-d_3 (Aldrich, 99.0% D) was dried over P_2O_5 and redistilled before use.

Tetra-*n*-butylammonium tris(hexafluoroacetylacetonato)ruthenate(II) was prepared from $Ru(hfac)_3^0$ (Strem Chemicals) by the method of Patterson and Holm,[10] except that *n*-Bu_4NBr (Eastman; recrystallized from water) was used in place of *n*-Bu_4NI; the product gave good elemental analyses.

Tris(acetylacetonato)chromium(III) ($Cr(acac)_3^0$) was made by the method of Fernelius and Blanch[11] (mp 217.3 °C; good elemental analyses).

NMR Measurements at Ambient Pressure. NMR spectra were taken with quadrature detection on a Bruker WH-90 spectrometer at 90 MHz against a deuterium oxide lock. For runs in the standard Bruker probehead at atmospheric pressure, a pulse width of 1.5 μs and sweep widths of ±800 Hz (Ru^{II}) or ±5000 Hz (Ru^{III}) were appropriate. All samples were made up by weight under an atmosphere of dry, oxygen-free nitrogen. Some reduction of $Ru(hfac)_3^0$ to $Ru(hfac)_3^-$ occurred in some cases, notably when acetone was the solvent (cf. ref 8). Accordingly, the actual mole fraction f_P of the total ruthenium concentration $[Ru]_T$ that was present in solution as the paramagnetic species $Ru(hfac)_3^0$ was determined for each kinetic measurement by measuring the frequency difference $\Delta\delta\nu$ between the methine ^1H resonance of diamagnetic $Ru(hfac)_3^-$ in the mixed solution and that of $Ru(hfac)_3^-$ alone in the same solvent (with excess tetra-*n*-heptylammonium iodide to suppress oxidation), with an internal frequency standard such as tetramethylsilane (TMS). This difference was then compared to the frequency difference $\Delta\nu$ between the ^1H resonances of $Ru(hfac)_3^0$ and $Ru(hfac)_3^-$ in separate solutions.

$$f_P = [Ru(hfac)_3^0]/[Ru]_T = \Delta\delta\nu/\Delta\nu \qquad (1)$$

The chemical shift of the methine protons of the Ru^{II} complex in $CDCl_3$ was 556.5 ± 0.2 Hz downfield from TMS, with full line width at half-maximum 1.35 ± 0.05 Hz (cf. 1.7 Hz reported[8]); the corresponding resonance of the Ru^{III} species was located 4418 ± 15 ($=\Delta\nu$) upfield of the Ru^{II} peak, with line width 205 ± 2 Hz. These values were independent of temperature over the range 14–36 °C. Similar results were obtained for the other solvents. It was established that the proton chemical shift of residual $CHCl_3$ in $CDCl_3$, at 645.1 Hz downfield of TMS, was independent of temperature, pressure, and the presence of the $Ru(hfac)_3^{0,-}$ reaction mixture, relative to TMS, and was used as the internal frequency standard for all kinetic measurements in chloroform. For kinetic measurements in the other solvents, 0.01 mol kg^{-1} benzene was added as the internal frequency standard rather than the more volatile TMS; again, it was shown that the proton chemical shift of benzene relative to TMS was unaffected by pressure *P*, temperature *T*, or the presence of the reactants.

NMR Measurements at Elevated Pressure. Spectra were obtained at pressures up to 200 MPa with a pressurizable probehead similar to that described previously[6] but with dimensions and matching circuit suitable for operation at 90 MHz. Samples were enclosed in glass tubes capped with a collapsible Teflon tube that was then stoppered and sealed with an epoxy cement. The pressurizing fluid was deoxygenated carbon tetrachloride.

Table I. Rate Constants and Enthalpies and Entropies of Activation for the $Ru(hfac)_3^{0,-}$ Electron-Transfer Reaction[a]

solvent	$[Ru]_T$/mol kg^{-1}	*k*/kg mol^{-1} s^{-1}	ΔH^*/kJ mol^{-1}	ΔS^*/J K^{-1} mol^{-1}
$(CD_3)_2CO$	0.03–0.09	1.04×10^7	17.6 ± 4.2[b]	−52 ± 14[b]
CD_3CN	0.03–0.06	5.3×10^6	16.8 ± 4.2[b]	−61 ± 14[b]
$CDCl_3$	0.006–0.01	1.11×10^7	24.5 ± 2.5	−28 ± 12
CD_3OD	0.02–0.085	6.2×10^6	21.8 ± 3.1	−41 ± 8

[a] 298.2 K; cation $(n\text{-}C_4H_9)_4N^+$. [b] Reference 8; all other data are from this work.

Analysis of the solution for $Ru(hfac)_3^0$ was made at 0.1 MPa according to eq 1, using the value of $\Delta\nu$ derived previously. Exchange rate measurements, however, required knowledge of the pressure dependences of the methine proton chemical shifts and line widths of both $Ru(hfac)_3^-$ and $Ru(hfac)_3^0$. These dependences could not be obtained directly for the latter (paramagnetic) complex in the relatively insensitive high-pressure probehead because of weakness of the broad signal (which derives from only three protons per molecule of this sparingly soluble compound) and the tendency, noted above, of the Ru^{III} to be slowly reduced, probably by impurities in the solvents. Accordingly, the pressure dependences of the line width and chemical shift of $Cr(acac)_3^0$ were measured in the selected solvents as a model for the expected behavior of $Ru(hfac)_3^0$, since the Cr^{III} complex is of similar size and shape, is very stable with respect to redox or ligand loss, and has 7 times as many protons (the NMR signals of which appear as a single broad envelope because of the strong paramagnetism).

Results

At ambient pressure, rate constants *k* for the $Ru(hfac)_3^{0,-}$ ET reaction were derived from the expression[8]

$$k = 4\pi f_P(1 - f_P)(\Delta\nu)^2/\{W_{DP} - (1 - f_P)W_D - f_PW_P\}[Ru]_T \qquad (2)$$

where W_{DP}, W_D, and W_P are the full widths at half-height of the methine proton resonances of $Ru(hfac)_3^-$ in the reaction mixture, $Ru(hfac)_3^-$ in solution alone, and $Ru(hfac)_3^0$ in solution alone, respectively. Equation 2 applies only in the "fast-exchange" limit and is appropriate here because, in all cases, $k[Ru]_T \gg 2\pi\Delta\nu$. Rate constants *k* were usually reproducible to 2–3%, but their absolute accuracy is probably only about ±10% because of their dependence on $\Delta\nu$ in the fast-exchange region. Ambient-pressure values of *k* are listed in the supplementary tables and, for 25 °C, in Table I. Agreement with the rate constants of Chan and Wahl[8] was very good (note the different concentration units). For variable-temperature studies of solutions in $CDCl_3$ and CD_3OD, linear Eyring plots were obtained, and the corresponding ΔH^* and ΔS^* values (which were not reported by Chan and Wahl[8]) are also given in Table I. In no case was a significant dependence of *k* upon $[Ru]_T$ observed.

For kinetic measurements at elevated pressures, the shim settings required small readjustments for each new pressure. Fortunately, it was found that the ^1H line width W_D in $Ru(hfac)_3^-$ in the absence of Ru^{III} was precisely linearly related (with unit slope) to the ^1H line widths of the internal standard $CHCl_3$ or C_6H_6 as the pressure was varied. Thus, accurate estimation of W_D could be made along with measurement of W_{DP} and $\Delta\delta\nu$ at each pressure.

The line width W_P of $Ru(hfac)_3^0$, however, could not be reliably measured in the high-pressure probehead. Accordingly, sets of ET rate constants *k* were calculated on two alternative assumptions: (1) that W_P is independent of pressure *P* and (2) that ln W_P varies linearly with *P*, with the same slope as does the logarithm of the line width of the more tractable paramagnetic solute $Cr(acac)_3^0$:

$$\ln W_P(P) = \ln W_P(0) + AP \qquad (3)$$

where the constant *A* (Table II) is assumed to be the same for $Ru(hfac)_3^0$ and for the Cr complex in a given solvent (the chemical shift of the protons in the Cr complex was unaffected by pressure within the experimental uncertainty of ±100 Hz). The second

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Table II. Pressure Dependence of the ^1H NMR Line Width of $Cr(acac)_3^0$ According to Eq 3[a]

solvent	$W_P(0)$/Hz	$A/10^{-3}$ Hz MPa^{-1}	chem shift[b]/Hz
$(CD_3)_2CO$	900	1.69 ± 0.07	3650 ± 20
CD_3CN	930	1.63 ± 0.09	3660 ± 20
$CDCl_3$	1300	0.91 ± 0.11	3750 ± 30
CD_3OD	1060	1.22 ± 0.04	3660 ± 30

[a] 24.9 °C, 0.1–200 MPa. [b] Downfield from TMS.

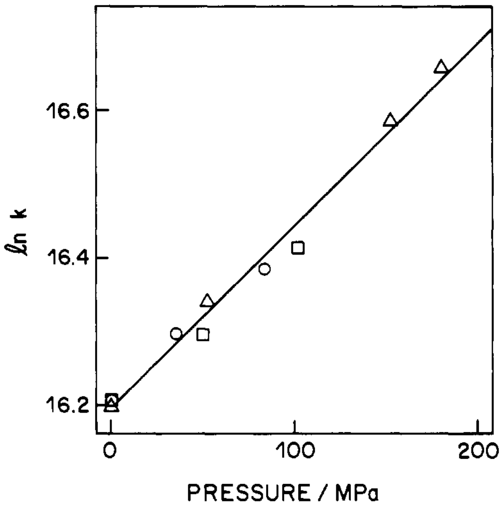

Figure 1. Pressure effect on the rate of the $Ru(hfac)_3^{0,-}$ exchange in acetone-d_6 at 24.8 °C. Total Ru concentrations/mol kg^{-1}: 0.0971 (circles); 0.0718 (triangles); 0.0375 (squares).

assumption is arbitrary, although the Debye equation[12] suggests that W_P should be proportional to η/T, where η is the viscosity of the solvent, and its dependence upon P should therefore be approximately log–linear[13] with $A = (\partial \ln \eta/\partial P)_T$. In fact, the A values of Table II are less than this would predict—e.g., for acetonitrile, $(\partial \ln \eta/\partial P)_T$ is about 3.25×10^{-3} MPa^{-1}.[14] This phenomenon, which reflects the pressure dependence of the factor $\varkappa$ introduced by McClung and Kivelson[15] to correct the Debye equation, seems to be rather general[16] and presumably arises because the intermolecular torques that control W_P increase more slowly with rising pressure than do intermolecular forces that determine η.[12]

Thus, A is expected to be controlled by the properties of the solvent rather than of the paramagnetic solute.[15] In any event, $Cr(acac)_3^0$ has essentially the same size, shape, and charge type as $Ru(hfac)_3^0$, although its t_{2g}^3 electronic configuration leads to NMR line widths some 5 times those of the t_{2g}^5 Ru^{III} complex (Table II).[17] The second assumption therefore represents a reasonable correction (or, at worst, an overcorrection) to W_P. Rate constants calculated on the assumption of a pressure-independent W_P are called k, and those based upon W_P values corrected as above are called k_{cor}. In general, k_{cor} was only slightly larger than k even at the highest pressures (e.g., for methanol, never more than 4.7% larger—see supplementary tables), but in the case of acetone the "correction" introduced excessive scatter that was not present in k. A downward drift in f_P with time (due to some loss of Ru^{III}) had been noted in some cases when line width measurements were made in acetone under pressure, however, and correction of these less reliable k values is considered redundant.

Plots of ln k (Figure 1, for acetone solvent) or ln k_{cor} (Figures 2–4) against pressure are essentially linear to within the experimental uncertainty; i.e., ΔV^* and ΔV_{cor}^* could be taken to be pressure-independent.

$$\ln k = \ln k_0 - P\Delta V^*/RT \qquad (4)$$

In fact, distinct curvature of the semilogarithmic plot is discernible at least in the case of methanol (Figure 4) and indeed is predicted by theory (see Discussion). Thus, the volumes of

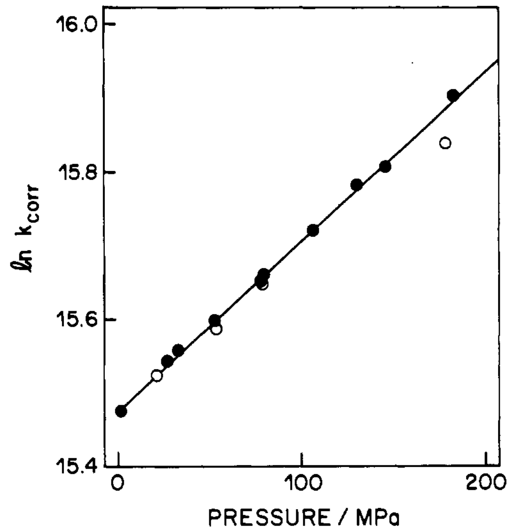

Figure 2. Pressure effect on the rate of the $Ru(hfac)_3^{0,-}$ exchange in acetonitrile-d_3 at 25.6 °C. Total Ru concentrations/mol kg^{-1}: 0.0592 (filled circles); 0.0325 (open circles).

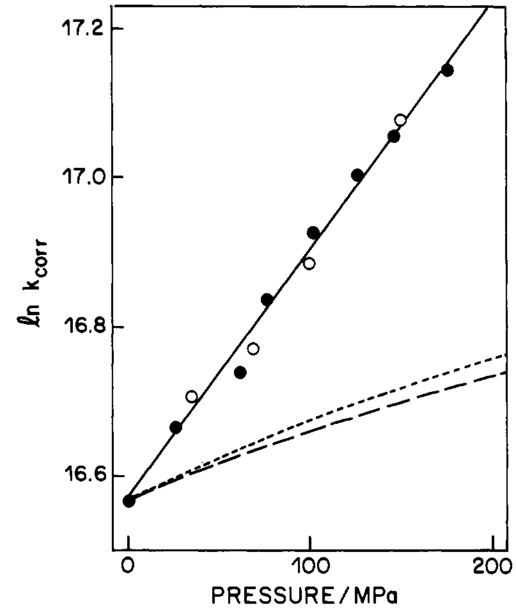

Figure 3. Pressure effect on the rate of the $Ru(hfac)_3^{0,-}$ exchange in chloroform-d at 25.9 °C. Total Ru concentrations/mol kg^{-1}: 0.00658 (filled circles); 0.00747 (open circles). Dotted curve: calculated effect if σ is pressure-dependent (includes pressure dependence of K_A). Dashed curve: calculated effect if σ is independent of pressure. ΔV_{IR}^* is assumed negligible.

Table III. Mean Volumes of Activation (0–200 MPa) for the $Ru(hfac)_3^{0,-}$ Exchange Reaction[a]

solvent	temp/°C	ΔV^{*b}/cm^3 mol^{-1}	ΔV_{cor}^{*c}/cm^3 mol^{-1}
$(CD_3)_2CO$	24.8	−6.1 ± 0.3	
CD_3CN	25.6	−4.1 ± 0.1	−5.5 ± 0.1
$CDCl_3$	25.9	−7.8 ± 0.2	−8.1 ± 0.2
CD_3OD	25.3	−5.2 ± 0.3	−5.8 ± 0.3

[a] Uncertainties are standard deviations of fit to eq 4. [b] From k uncorrected for pressure dependence of W_P. [c] Corrected for estimated pressure dependence of W_P.

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(17) Swift, T. J. In *NMR of Paramagnetic Molecules*; Lamar, G. N., Horrocks, W. DeW., Jr., Holm, R. H., Eds.; Academic: New York, 1973; p 53.

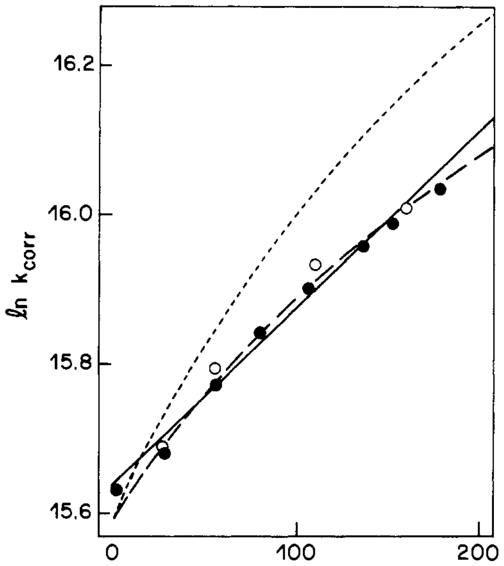

Figure 4. Pressure effect on the rate of the $Ru(hfac)_3{}^{0,-}$ exchange in methanol-d_4 at 25.3 °C. Total Ru concentrations/mol kg^{-1}: 0.0601 (open circles); 0.0258 (filled circles). Solid line: linear fit of the data. Dotted curve: calculated effect if σ is pressure-dependent (includes pressure dependence of K_A). Dashed curve: calculated effect if σ is independent of pressure. $\Delta V_{IR}{}^*$ is assumed negligible.

activation listed in Table III should be regarded as *mean* values for the experimental pressure range of 0.1–200 MPa. For the data obtained in acetonitrile, chloroform, and methanol, the effect on ΔV^* (Table III) of the adjustment of k for the estimated pressure dependence of W_P turns out not to be large, and the corrected volumes of activation $\Delta V_{cor}{}^*$ are taken to be definitive. For the acetone case, a provisional value of -6 ± 1 cm^3 mol^{-1} is adopted for the mean volume of activation. In the following discussion, k and ΔV^* are taken to mean k_{cor} and $\Delta V_{cor}{}^*$, respectively, wherever the latter are definitive.

Discussion

In current practice,[18] the classical Marcus–Hush expressions for the rate constant k of outer-sphere ET are taken to include the stability constant K_A of the putative precursor complex formed by the reactants and the transmission coefficient κ_{el} (which may be less than unity because of electronic effects on activation barrier crossing).

$$k = (K_A \kappa_{el} \nu_n) \exp(-\Delta G^*/RT) \qquad (5)$$

Here, ΔG^* is the free energy of activation, ν_n is the nuclear frequency (which we replace by the factor k_BT/h of transition state theory), and the other symbols have their usual SI meanings. In the present case, where one of the reactants is uncharged, K_A can be taken to be $4000\pi N\sigma^3/3$ in SI units if σ is the reactant separation (of the order of the sum of the reactant radii r_1 and r_2) at which ET is most probable and ΔG^* is the sum of the internal (metal–ligand) and solvent rearrangement free energies, $\Delta G_{IR}{}^*$ and $\Delta G_{SR}{}^*$, respectively. In the absence of vibrational force constant data for $Ru(hfac)_3{}^{0,-}$, $\Delta G_{IR}{}^*$ cannot be realistically predicted from theory,[18] but this is immaterial as far as pressure effects are concerned (see below), and $\Delta G_{IR}{}^*$ should be independent of changes of solvent. For the $Ru(hfac)_3{}^{0,-}$ ET reaction, the possible effects of solvent dynamics (dielectric relaxation) on the activation parameters can be ignored.[9,19] Furthermore, the reactants are quite large ($r_1 = r_2 = r = 0.5$ nm approximately),[8] so that the "two-sphere" continuous dielectric model[6] should be adequate. Quantum effects on the reaction rates should be unimportant, since the thermodynamic driving force is small.[20] Thus we have, in SI units[2-4,6]

$$\Delta G_{SR}{}^* = (Ne^2/16\pi\epsilon_0)(r^{-1} - \sigma^{-1})(n^{-2} - D^{-1}) \qquad (6)$$

where D is the static relative permittivity (dielectric constant) and n the refractive index (here taken, of practical necessity, to be at the conventional wavelength of 589.3 nm rather than at the ET frequency) of the solvent. It is usual to express the pressure dependence of k in terms of a volume of activation ΔV^*

$$(\partial \ln k/\partial P)_T = -\Delta V^*/RT \qquad (7)$$

with the expectation that ΔV^* will often be essentially independent of P, i.e., that $\ln k$ will be a linear function of P. The experimental data for the $Ru(hfac)_3{}^{0,-}$ ET reaction appear to conform to this expectation (Figures 1–4). This may, however, be illusory. From eq 6, we have[6]

$$\Delta V_{SR}{}^* = (Ne^2/16\pi\epsilon_0)(r^{-1} - \sigma^{-1})[(\partial n^{-2}/\partial P)_T - (\partial D^{-1}/\partial P)_T] \qquad (8)$$

if σ is regarded as pressure-independent, or if σ varies with pressure according to the isothermal compressibility β of the solvent

$$(\partial \ln k/\partial P)_T = (\partial \ln K_A/\partial P)_T - \Delta V_{SR}{}^*/RT = -\beta - \Delta V_{SR}{}^*/RT \qquad (9)$$

where

$$\Delta V_{SR}{}^* = (Ne^2/16\pi\epsilon_0)\{(r^{-1} - \sigma^{-1})[\partial(n^{-2} - D^{-1})/\partial P]_T - (n^{-2} - D^{-1})\beta/3\sigma\} \qquad (10)$$

and the contribution $\Delta V_{IR}{}^*$ of internal reorganization to ΔV^* has been ignored because it is known to be small for rigid molecules (following Stranks, we estimate $\Delta V_{IR}{}^* \sim +1$ cm^3 mol^{-1} in the present case).[3]

Pressure Dependence of Solvent Properties. The evaluation of eq 9 and 10 is critically dependent upon accurate knowledge of the pressure dependence of n, but this is available for only two of the solvents for which ET pressure studies were possible—chloroform and methanol.[21] To a first approximation, $n - 1$ can be taken as being proportional to the solvent density ρ,[6,22] which is conveniently represented by the modified Tait equation

$$1 - (V/V_0) = C \ln(1 + P/B) \qquad (11)$$

where V is solvent volume, the subscript zero refers to ambient pressure (which is negligible), and the constants B and C (Table IV) are available from Isaacs' compendium[23] or, in the case of methanol, can be computed from the compression data of Bridgman.[24] Vedam,[21,25,26] however, has shown on both theoretical and statistical grounds that the pressure dependences of both n and D are better expressed as polynomials in terms of the Eulerian strain

$$E = [1 - (V_0/V)^{2/3}]/2 \qquad (12)$$

which can in turn be calculated from eq 11. For our purposes, we can write with sufficient accuracy

$$n - n_0 = -\xi E \qquad (13)$$

and values of the proportionality constant ξ, calculated from the data of Vedam[21] using compressions obtained from eq 11, are given in Table IV. There is, unfortunately, no means of reliably predicting ξ for solvents for which measurements of n at high pressure have not been made (for water, ξ is very close to unity, but this is evidently fortuitous). The pressure dependence of D can be handled in much the same way,[26] but it is sufficient to use the Tait-like equation

$$1 - (D_0/D) = C'D_0 \ln(1 + P/B') \qquad (14)$$

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Table IV. Parameters That Govern the Pressure Dependence of the $Ru(hfac)_3^{0,-}$ Exchange Rate in Chloroform and Methanol[a]

		param values	
param	press/MPa	chloroform at 25 °C	methanol at 20 °C
B/MPa		105.2[b]	99.4[c]
C		0.1038[b]	0.1029[c]
ξ		1.4674	1.1368
n	0.1	1.444 70[d]	1.329 88[d]
	100	1.4807	1.3588
	200	1.5043	1.3774
$(\partial n^{-2}/\partial P)_T/10^{-10}$ Pa^{-1}	0.1	−3.20	−3.34
	100	−1.718	−1.765
	200	−1.188	−1.218
D	0.1	4.716[e]	33.60[f]
	100	5.116	36.54
	200	5.365	38.43
B'/MPa		80.3[e]	87.5[f]
C'		0.020 51[e]	0.003 146[f]
$(\partial D^{-1}/\partial P)_T/10^{-10}$ Pa^{-1}	0.1	−2.55	−3.60
	100	−1.138	−1.678
	200	−0.732	−1.094
$\beta/10^{-10}$ Pa^{-1}	0.1	9.87	10.35
	100	5.44	5.56
	200	3.82	3.88
ΔV_{SR}^*/cm^3 mol^{-1} [g]	0.1	−2.2	−10.4
	100	−2.0	−5.5
	200	−1.6	−3.9
ΔV_A/cm^3 mol^{-1} [h]	0.1	+2.4	+2.5
	100	+1.3	+1.4
	200	+0.9	+0.9
$\Delta V_{SR}^{*\prime}$/cm^3 mol^{-1} [h]	0.1	−5.3	−16.8
	100	−3.7	−8.9
	200	−2.7	−6.1

[a] See text. [b] Reference 23. [c] From least-squares fit of data of ref 24. [d] Reference 21. [e] Extrapolated from data for 30 and 50 °C, ref 27. [f] Reference 27. [g] Reactant separation $\sigma = r_1 + r_2 = 1.0$ nm, independent of pressure. [h] $\sigma = r_1 + r_2 = 1.0$ nm at 0.1 MPa but is pressure-dependent—see text.

for which the parameters B', C', and D_0 are available.[27] Thus we have

$$(\partial n^{-2}/\partial P)_T = -2n^{-3}(\partial n/\partial P)_T \tag{15}$$

$$n = n_0 - (\xi/2)\{1 - [1 - C \ln (1 + P/B)]^{-2/3}\} \tag{16}$$

$$(\partial n/\partial P)_T = [(\xi C/3)(B + P)][1 - C \ln (1 + P/B)]^{-5/3} \tag{17}$$

$$(\partial D^{-1}/\partial P)_T = -C'/(B' + P) \tag{18}$$

$$\beta = C/\{(P + B)[1 - C \ln (1 + P/B)]\} \tag{19}$$

As Table IV clearly shows, eq 15–19 generate strongly pressure-dependent values for the key parameters in eq 10—thus, ΔV_{SR}^* necessarily becomes markedly less negative as the pressure is increased, and curvature of the ln k vs P plot for these and other ET reactions in solution is to be expected. We have pointed this out previously with reference to the $MnO_4^{-,2-}$ reaction in water;[6] in the present cases involving nonaqueous solvents, however, the low values of the Tait constants B relative to our 200-MPa pressure range (Table IV; cf. 300 MPa for water at 25 °C) produce a more marked pressure dependence of ΔV_{SR}^* and hence of ΔV^* (since ΔV_{IR}^*, even if it were not negligible in itself, is unlikely to be significantly pressure-dependent[3]).

Reaction in Methanol. The expected nonlinearity of the ln k vs pressure plot is indeed perceptible for methanol in Figure 4 and in fact can be accounted for quite realistically by calculating k/k_0 values from eq 6 with the naive assumptions that $\sigma = 2r = 1.0$ nm and is independent of pressure (the calculations are made for 20 °C, for which all the required parameters are available, rather than the experimental temperature of 25 °C, but the discrepancy in pressure effects is insignificant). If σ is acknowledged to vary with pressure along with the compression of the solvent, the contribution of solvent rearrangement to ΔV^* (as represented in Table IV by $\Delta V_{SR}^{*\prime}$) becomes too great and the curvature too sharp. This is offset to some extent by the opposing effect of the pressure dependence of σ on K_A (eq 5); as shown elsewhere,[6] the corresponding contribution ΔV_A to ΔV^* ($=\Delta V_{IR}^* + \Delta V_{SR}^{*\prime} + \Delta V_A$) is given by βRT (Table IV). In short, if ΔV_{IR}^* is negligible, eq 8 accommodates the data for methanol better than does eq 10, as Figure 4 shows. This could be taken to mean that ET occurs only on direct contact of $Ru(hfac)_3^0$ on $Ru(hfac)_3^-$ and that these behave as hard spheres, as in the simplest version of the SHM theory. The calculations are, however, somewhat dependent upon the choice of values for r and σ, and a version that incorporates a pressure dependence of σ (eq 9 and 10) is not ruled out. Comparison of Tables III and IV shows that SHM theory accounts adequately for the observed mean ΔV^* for the $Ru(hfac)_3^{0,-}$ exchange in methanol if ΔV_{IR}^* is indeed small (1 ± 1 cm^3 mol^{-1}), and our rough theoretical estimations of ΔV_{IR}^* in the manner of Stranks[3] confirm this.

Reaction in Acetone and Acetonitrile. For acetone (Figure 1), the expected curvature in the ln k vs pressure plot may be masked by scatter of the data, although the plot for acetonitrile (Figure 2) seems to be truly linear. Unfortunately, in neither case is the pressure dependence of n known, although the other parameters in eq 6–19 are available,[23,27–29] and the extent of the curvature of the ln k vs pressure plot cannot be predicted. The mean values of ΔV^* over the 0–200-MPa experimental pressure range (Table III) are, however, similar for acetone, acetonitrile, and methanol, which is reasonable since the physical properties of these solvents are not widely different. Thus, if it is accepted that SHM theory or a variant of it adequately represents the experimental results for methanol as solvent, then the same may be taken to hold for the solvents acetone and acetonitrile.

Reaction in Chloroform: Role of Ion Pairing. For chloroform, the mean ΔV^* is markedly more negative than for the other solvents (Table III), which is the opposite of the prediction of eq 6–19; terms involving D^{-1} come close to compensating those involving n^{-2} for this solvent, and $|\Delta V^*|$ should be small (Table IV). Figure 3 shows that the curved ln k vs pressure plots predicted on the basis of eq 6–19 are grossly in disagreement with experiment. This cannot be due to our neglect of ΔV_{IR}^*, for which a small *positive* value is anticipated. The most likely explanation is that, because of the very low relative permittivity of chloroform, there is extensive ion pairing between $Ru(hfac)_3^-$ and Bu_4N^+

$$Ru(hfac)_3^- + Bu_4N^+ \rightleftharpoons \{Ru(hfac)_3^-,Bu_4N^+\} \tag{20}$$

which depletes the reactive pool of the Ru^{II} species and results in slower ET rates; pressure favors breakup of ion pairs[30] and therefore accelerates the reaction. Chan and Wahl[8] note, and our data confirm, that the $Ru(hfac)_3^{0,-}$ exchange is at least an order of magnitude slower than would be predicted from the trend of the rates in other solvents, and they, too, suggest that ion pairing is extensive in chloroform (though the effect seems not to be so important in other solvents of low relative permittivity).

The formation constant K_{IP} for the ion pair $\{Ru(hfac)_3^-,Bu_4N^+\}$ can be estimated from the Fuoss equation[30]

$$K_{IP} = (4000\pi Na^3/3) \exp b \tag{21}$$

where a is the distance of closest anion–cation approach and

$$b = |z_1 z_2| e^2/4\pi\epsilon_0 k_B T a D \tag{22}$$

where z_1 and z_2 are the respective ionic charges. For chloroform at 298 K and 0.1 MPa, with an estimated a value of 1.0 nm, we calculate $K_{IP} = 3.6 \times 10^5$ L mol^{-1}. This means that, at the Ru^{II} concentrations of our experiments, ion pairing will be almost

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(27) Reference 23, p 99 (for logarithms to base 10; note also that eq 2.61 on p 98 gives the negative of the left-hand term, so that Isaacs' function Φ is negative).

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Table V. Calculated Contributions to the Free Energy of Activation for the $Ru(hfac)_3{}^{0,-}$ Exchange

solvent	$\Delta G^{*\,a}$/kJ mol^{-1}	ΔG_{SR}^*/kJ mol^{-1}	$\Delta G_{IR}^{*\,b}$/kJ mol^{-1}
acetone	33.0	17.0	16.0
acetonitrile	34.6	18.3	16.3
chloroform	32.8	9.4	*c*
methanol	34.3	18.6	15.7

[a] Calculated from the experimental *k* values of Table I, with the assumption that $\kappa_{el} = 1$. [b] Assume $\Delta G^* = + \Delta G_{SR}^*$. [c] Ion pairing dominant.

complete, and the concentration of free $Ru(hfac)_3{}^-$ will be $([Ru^{II}]_T/K_{IP})^{1/2}$. Thus, if only the free cation is involved in the ET reaction, we have

$$\Delta V^* = \Delta V_{IR}^* + \Delta V_{SR}^* - 0.5\Delta V_{IP} \tag{23}$$

where ΔV_{IP}, the volume change for ion-pair formation, is given by $-|z_1z_2|(Ne^2/4\pi\epsilon_0 a)(\partial D^{-1}/\partial P)_T$. Table IV shows that $(\partial D^{-1}/\partial P)_T$ varies with pressure and hence so must ΔV_{IP}, but for the midpoint of our pressure range, $\Delta V_{IP} = +15.8$ cm^3 mol^{-1}, so that eq 23 accounts for the observed mean ΔV^* value if ΔV_{IR}^* is about +2 cm^3 mol^{-1} (cf. 1 ± 1 cm^3 mol^{-1} estimated above for methanol solutions) and the anticipated curvature of the ln *k* vs pressure plot is obscured by the experimental uncertainty. Confirmation of the proposed ion-pair effect requires demonstration of a dependence of *k* on $[Ru^{II}]_T{}^{1/2}$ or on $1/[Bu_4N^+]$, but the limitations imposed by solubility and NMR sensitivity prevented this.

For acetone, acetonitrile, and methanol, the calculated values of K_{IP} at 298 K are 47, 12, and 13 L mol^{-1}, respectively, so that no more than 5% ion pairing between $Ru(hfac)_3{}^-$ and Bu_4N^+ is predicted to have occurred in acetone at the highest $[Ru^{II}]$, and much less in all other cases.

Free Energy of Activation. The calculated contributions ΔG_{SR}^* of solvent rearrangement to the free energy of activation are collected in Table V, together with ΔG^* values derived from the experimental *k*'s on the assumption that $\kappa_{el} = 1$. This assumption is reasonable because any significant degree of nonadiabaticity (i.e., $\kappa_{el} \ll 1$) would make a significant *negative* contribution to ΔV^*,[6] whereas even the simplest version of the SHM theory already errs on the negative side of the experimental ΔV^* values (exclusive of the small ΔV_{IR}^* component). The difference $\Delta G^* - \Delta G_{SR}^* = 16.0 \pm 0.3$ kJ mol^{-1} is remarkably constant for three of the solvents (for $CDCl_3$, ion pairing obscures the issue) and may be taken to be ΔG_{IR}^*. A similar dissection of ΔH^* and ΔS^* into internal and solvent reorganizational contributions would be unrealistic because of the large experimental uncertainties (Table I); the Marcus theory, however, would predict $\Delta H_{IR}^* \sim \Delta G_{IR}^*$.[2]

Conclusions. The SHM theory provides a satisfactory basis for rationalization of pressure effects on the rates of the $Ru(hfac)_3{}^{0,-}$ ET reaction in acetone, acetonitrile, and methanol, insofar as the required physical parameters of the solvents are available and the assumed values of the effective radii *r* and optimum separation σ of the reactants are realistic. The reaction in chloroform behaves in accordance with nearly complete association of $Ru(hfac)_3{}^-$ with its counterion to form a relatively unreactive ion pair but is otherwise consistent with SHM theory. In the absence of ion pairing, the kinetic effects of pressure are largely determined by the solvent rearrangement terms, but internal rearrangement of the reacting complexes appears to make a significant contribution to ΔG^*.

Comparison of these findings with those of the very thorough studies by Wherland and co-workers[32,33] of the $Mn(CNR)_6{}^{+,2+}$ series of self-exchange reactions in various solvents is instructive; the effects of ion association are much more evident with the manganese isocyano complexes, as expected, while solvent effects correlate poorly with predictions of the Marcus–Hush theory, and a wide range of ΔV^* values is observed as R is varied, strongly negative values being associated with flexible R groups. The latter effect is unlikely to arise with complexes of the relatively rigid hfac$^-$ ligand, and it would seem that comparatively simple derivatives of the Marcus–Hush theory may be adequate when dealing with ET in a variety of solvents between large, rigid species of low charge such as $Ru(hfac)_3{}^{0,-}$, so long as association with the counterion(s) is not significant.

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Supplementary Material Available: Tables of NMR shifts, line widths, and rate constants at variable temperature in chloroform and methanol and a table of values of *k* and k_{cor} as functions of pressure for all solvents (3 pages). Ordering information is given on any current masthead page.

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