same symmetry and geometry as the $[Ru_2(NH_3)_6X_3]^{2+}$ complexes, and so the same qualitative molecular orbital scheme can be used to describe their transition energies. Assigning the peaks by analogy with $[Ru_2(NH_3)_6X_3]^{2+}$ gives good agreement with those proposed by Heath et al.[15] Again, the strength of the Ru-Ru interaction can be estimated from the two lowest energy peaks, and it is also expected that Δ for the nonahalides will be lower than Δ for the $[Ru_2(NH_3)_6X_3]^{2+}$ complexes. The transition energies depend on the Ru-Ru interaction as well as the ligand field strength. It is therefore possible to estimate the differences in the ligand field splittings between $[Ru_2(NH_3)_6X_3]^{2+}$ and $[Ru_2X_9]^{4-}$ and thus test the validity of the assignments. To fit the band positions for $[Ru_2Cl_9]^{4-}$ and $[Ru_2Br_9]^{4-}$ with $[Ru_2(NH_3)_6Cl_3]^{2+}$, Δ has to be reduced by a factor of $^3/_4$ and $^2/_3$, respectively. On changing the RuN_3Cl_3 chromophore to RuX_6, the change in Δ can be estimated from the spectrochemical *f* factors[14] to be 0.78 for X = Cl and 0.70 for X = Br. These values compare well with the estimated values of 0.75 and 0.67. Therefore, the proposed set of assignments for these ruthenium blues provides a good basis for the understanding of their electronic spectra.

Another related system recently studied[16] is the complex $[Ru_2L_2(\mu\text{-}Cl_3)]^{2+}$ (L = 1,4,7-triazacyclononane). The electronic absorption band positions have been reported, and they are virtually identical with those for the $[Ru_2(NH_3)_6Cl_3]^{2+}$ complex.

Conclusion

The results obtained in this study confirm the conclusions of the earlier RR study of these complexes. In addition, the depolarization ratios measured over a wide range of exciting lines are entirely consistent with the visible absorption (centered at 17 000 and 15 900 cm^{-1} for the chloro and bromo complexes, respectively) being assigned as the *z*-polarized electronic transition, $\sigma \rightarrow \sigma^*$. There is also strong evidence for the weaker transition at 23 000 and 22 100 cm^{-1} for the chloro and bromo complexes, respectively, being assigned as the *x*,*y*-polarized transition $\sigma^* \rightarrow \pi^*$.

The energies of the two transitions $\sigma \rightarrow \sigma^*$ and $\sigma^* \rightarrow \pi^*$, as well as the energy of the near-IR transition ($\delta^* \rightarrow \sigma^*$), have been used to assign the remaining absorption bands in the electronic spectra. Thus, all of the allowed transitions between the states derived from metal d orbitals have been assigned to bands observed in the electronic spectra of $[Ru_2(NH_3)_6Cl_3]^{2+}$ and $[Ru_2(NH_3)_6Br_3]^{2+}$. The same ordering of transition energies can be used to give a reasonable set of assignments for the spectra of other related ruthenium blues. This confirms the appropriateness of the assignments using the molecular orbital scheme of Figure 1.

There remains the question of the relation of these assignments to the MCD spectra published. Agreement between the RR and MCD results can only be obtained if it is assumed that the *x*,*y*-polarized transition does not cause significant resonance enhancement of any Raman band. This would be unusual behavior for a strongly allowed electronic transition. Furthermore, the main visible absorption band is highly symmetric, suggesting that it derives only from a single electric dipole allowed transition. The MCD results indicate that the absorption derives from at least two transitions, with the dominant transition, $\delta \rightarrow \pi$ (*x*,*y*-polarized), lying on the low-energy side of the absorption maximum. Thus, the RR experiments and the profile of the main visible absorption band are not consistent with the MCD results. Further investigation of the MCD spectra is required to rationalize these discrepancies.

Acknowledgment. We wish to thank Dr. Brendan J. Kennedy for access to unpublished results[15] and Patricia Del Favero, formerly of the Department of Inorganic Chemistry of the University of Sydney, for initial discussions concerning synthetic methods and also for supplying the unpublished data on the iodo complex. This work was supported by the Australian Research Grants Scheme.

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Solvent and Temperature Dependences of the Osmocene(II)/Iodoosmocene(IV) Atom/Electron Exchange

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The rates of the atom/electron exchange process between $OsCp_2$ and $OsCp_2I^+$ as the $CF_3SO_3^-$ salt (Cp represents the cyclopentadienide anion) have been measured by ^1H NMR line broadening as a function of temperature in nine solvents. The apparent second-order rate constants at 20 °C and the activation parameters are given. The rate constant, enthalpy of activation, and entropy of activation range from 1.0×10^3 M^{-1} s^{-1}, 2.1 kcal/mol, and −38 cal/(mol K) in tetrahydrofuran-d_8 to 78.3×10^3 M^{-1} s^{-1}, 11.3 kcal/mol, and 3 cal/(mol K) in acetone-d_6. Concentration studies, varying both Os(II) and Os(IV) concentration, show that there is a significant deviation from simple second-order behavior in chloroform-d_1 and methylene-d_2 chloride. Similar behavior for the analogous reaction of $RuCp_2/RuCp_2I^+$ was attributed to ion pairing, but such an analysis cannot fully explain the results obtained here. Instead, the data conform to a rate law with parallel paths, one that is overall second order and another that is independent of $OsCp_2I^+$ and first order in $OsCp_2$. Such an analysis is also consistent with the previous results for the $RuCp_2/RuCp_2I^+$ reaction. Conductivity studies establish that ion association occurs in the low dielectric constant solvents chloroform-d_1, methylene-d_2 chloride, bromobenzene-d_5, and tetrahydrofuran-d_8. Ion-pair formation constants for $[OsCp_2I]CF_3SO_3$ in methylene chloride at 20 and 35 °C are 4.2×10^5 M^{-1} and 3.8×10^5 M^{-1}, respectively. The analogous pentamethylcyclopentadienide system does not show exchange on the time scale of the NMR experiment.

Introduction

Recently, we reported kinetic studies on the atom/electron transfer reaction between $RuCp_2$ and $RuCp_2X^+$ (X = Br, I) in various solvents.[2] This reaction type generally contrasts with simple one-electron outer-sphere electron-exchange reactions, since atom transfer (e.g. transfer of halides) is involved and mechanistically several pathways are possible. Questions such as whether zero-, one-, or a concerted two-electron transfer occurs and whether bridged intermediates such as $[RuCp_2\text{-}X\text{-}RuCp_2]^+$ are involved and, if so, what their lifetime and electron distribution are have to be asked.

Variation of halide, metal, anion, and the use of pentamethylcyclopentadienide, as well as solvent-, temperature-, pressure-, and concentration-dependence studies, may help to elucidate the reaction mechanisms. Comparisons with recent

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Table I. Activation Parameters and Observed Second-Order Rate Constants at 20 °C for the $OsCp_2/[OsCp_2I]CF_3SO_3$ System in Various Solvents

solvent (ϵ)	no. of pts	temp range, ±1 °C	Os(II)/OS(IV) concn, mM	ΔH^*,[b] kcal/mol	ΔS^*,[b] cal/(mol K)	$10^{-3}k$,[a] $M^{-1}\ s^{-1}$
$(CD_3)_2SO$ (46.7)	18	20 to 60	3.3/6.9 3.7/4.3	12.5 ± 0.3	0.3 ± 0.9	3.5
$(CD_3)_2CO$ (20.7)	13	−20 to 40	2.8/2.8	11.3 ± 0.2	2.5 ± 0.6	78.3
CD_3CN (37.5)	13	−20 to 70	7.9/7.8	7.6 ± 0.1	−13.3 ± 0.3	17.6
CD_3NO_2 (35.8)	5	0 to 40	7.9/5.6	7.1 ± 0.2	−13.9 ± 0.6	31.3
$C_6D_5NO_2$ (34.8)	9	10 to 90	8.5/6.9	6.6 ± 0.1	−15.3 ± 0.3	31.7
CD_2Cl_2 (8.9)	14	−30 to 30	12.7/11.2	6.1 ± 0.1	−16.8 ± 0.4	38.1
$CDCl_3$ (4.7)	17	−30 to 55	4.6/3.3	4.8 ± 0.1	−27.0 ± 0.3	2.0
C_6D_5Br (5.4)	10	0 to 40	3.6/0.8	4.7 ± 0.3	−25.5 ± 0.9	5.2
C_4D_8O (7.5)[c]	9	20 to 60	2.9/2.4	2.2 ± 0.1	−37.5 ± 0.4	1.0

[a] Apparent second-order rate constants measured at 20 °C (see text). [b] Calculated from the apparent second-order rate constants. [c] Tetrahydrofuran.

reports on kinetic investigations of other coupled atom/electron transfer systems should also prove to be interesting in this regard.[3,4]

In the present paper we continue our studies on such reactions and report on an investigation of the kinetics for various temperatures and solvents for the osmocene(II)/iodoosmocene(IV) atom/electron exchange reaction.

Experimental Section

Materials. Osmocene and decamethylosmocene were obtained from Strem Chemicals, Inc., and used without further purification. $[OsCp_2I]CF_3SO_3$ and $[Os(CpMe_5)_2I]CF_3SO_3$ were synthesized according to refs 5 and 6. Anal. Calcd for $[C_{10}H_{10}IOs]CF_3SO_3$: C, 22.15; H, 1.69; I, 21.27; S, 5.37. Found: C, 22.32; H, 1.71; I, 22.85; S, 5.74. Microanalysis was done by Galbraith Laboratories. All solvents used for the purification of both compounds were purchased from J. T. Baker Chemicals and purified by using standard procedures.[7] All solvents used for the NMR measurements were deuterated. They were purchased from MSD Isotopes and dried over 4-Å molecular sieves.

In the kinetic experiments the concentration of each of the reactants was varied from about 0.37 to 14 mM depending on solubility constraints.

^1H NMR Experiments. The data were recorded on a Nicolet NT200WB instrument operating at 200 MHz with acquisition parameters as described before.[2,8] Temperature was controlled within ±1 °C by using the built-in gas-flow temperature controller. Temperature readings were calibrated against the temperature dependence of the proton chemical shifts of acidified methanol.[9] For all measurements, tetramethylsilane (TMS) was used as a reference. Data analyses were carried out as previously described.[2,8,10] The temperature-dependence data were fit to the Eyring equation by using the linear least-squares method. The errors reported were derived from the scatter of the second-order rate constant, *k*, about the fit line. Estimated errors are about 3 times greater than these.

Conductivity Experiments. Conductivity experiments were run at the Technical University of Vienna in a thermostated cell with a cell constant of 0.43 cm^{-1} at 25 °C. The cell constant was measured by using aqueous KCl solutions. Cell resistance was measured with a Wayne-Kerr Autobalance University Bridge B 642 using a Pt electrode at 25.0 ± 0.1 °C.

Results

The proton NMR spectra of $OsCp_2$ show one line at δ 4.71 ppm vs TMS in all solvents used. The full width at half-height is 0.20 ± 0.05 Hz. The spectra of $[OsCp_2I]CF_3SO_3$ show one line. The full widths at half-height (varying from 0.2 to 0.8 Hz depending on solvent) and shifts (varying from 5.477 to 6.260 ppm depending on solvent) of $[OsCp_2I]CF_3SO_3$ are given in supplementary material Table 10. Both line widths and chemical shifts are independent of temperature in the range −30 to +90 °C.

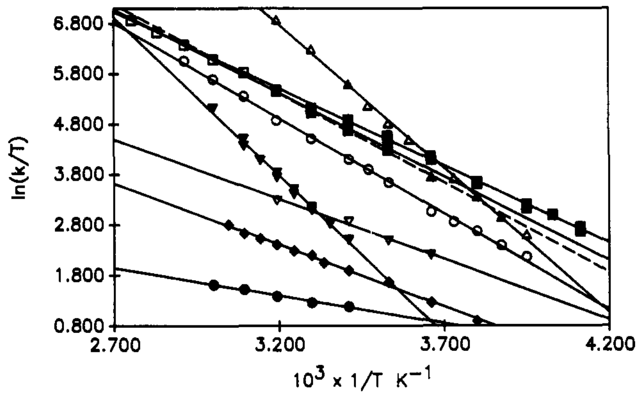

Figure 1. Eyring plot for the $OsCp_2/[OsCp_2I]CF_3SO_3$ electron exchange in different solvents: (○) acetonitrile; (▲) nitromethane; (□) nitrobenzene; (▼) dimethyl sulfoxide; (△) acetone; (■) methylene chloride; (◆) chloroform; (▽) bromobenzene; (●) tetrahydrofuran).

In accord with the analogous Ru system, it was found that the decamethyl derivatives of osmocene(II) and iodoosmocene(IV) do not show exchange. An upper limit of *k*, on the basis of the resolution of the NMR spectrometer due to field inhomogeneity (≤0.2 Hz) and the solubility of the complexes (ca. 20 mM in acetonitrile), can be estimated to be ca. 25 ± 5 $M^{-1}\ s^{-1}$ at 20 °C. At higher temperatures, depending on the solvent, decomposition occurred and precluded extending the temperature range. For instance, in the strong donor solvents acetone, dimethyl sulfoxide, and tetrahydrofuran, decomposition of $[OsCp_2I]CF_3SO_3$ occurs at temperatures higher than 60 °C. The results of the temperature-dependence measurements are given in Table I and Figure 1.

The rate was studied as a function of concentration in the solvents dimethyl sulfoxide, nitrobenzene, chloroform, and methylene chloride at 20 °C (given in supplementary material Tables 11–14). The low solubility of the charged complex in bromobenzene and tetrahydrofuran did not permit a concentration-dependence study. In the high dielectric constant solvents, dimethyl sulfoxide and nitrobenzene, the rate constants do not appreciably change when reactant concentration is varied and the second-order rate law is valid. In the low dielectric constant solvents, the apparent second-order rate constant increases as the concentration of Os(IV) decreases. There is no effect on the rate constants of changing the $OsCp_2$ concentration. The concentration-dependence data are presented as a plot of the apparent second-order rate constant vs [Os(IV)] in Figure 2. The data for the previously studied $RuCp_2/RuCp_2I^+$ reaction are included for comparison.

The conductance data were fit by means of a nonlinear least-squares program, minimizing χ^2, to a Fuoss–Kraus equation.[11] In the preceding paper,[2] the conductance data were also

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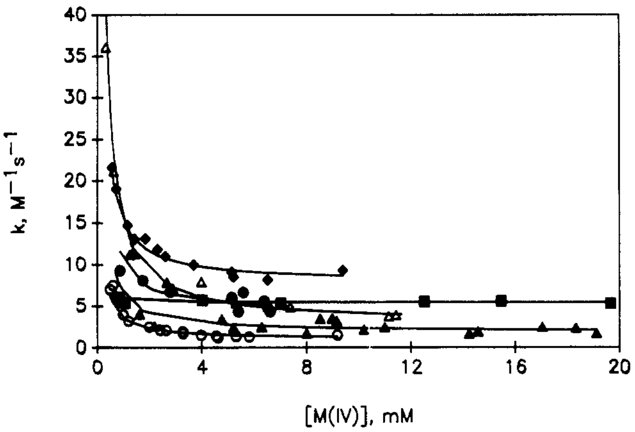

Figure 2. Test of the second-order rate law. Apparent second-order rate constants, k, are plotted vs [M(IV)]. The filled symbols represent the Ru reaction, and the open symbols represent the Os reaction. The solvents and reaction temperatures are (○, ◆) chloroform at 20 °C, (●) chloroform at −20 °C, (△, ▲) methylene chloride at 20 and −50 °C, respectively, and (■) acetonitrile at −30 °C. The rate constants have been multiplied by 10^{-4} in all cases except for the Os reaction in chloroform and the Ru reaction in chloroform at 20 °C, which have been multiplied by 10^{-3}.

Table II. Conductivity Data for $[OsCp_2I]CF_3SO_3$ in Methylene Chloride and Chloroform at Various Temperatures ($\mu = 0$)

solvent	T, °C	K^{0Xip},^{a} M^{-1}	λ_0,^{a} cm^2 mho mol^{-1}
$CHCl_3$	20	large^b	small
CH_2Cl_2	20	4.2×10^5	76.1
CH_2Cl_2	35	3.8×10^5	78.5

^{a}Data were fit to the Fuoss–Kraus equation.[11] Errors in K_{ip}^0 are estimated to be 25‰. ^{b}Too large to measure.

fit to the more general Fuoss–Hsia equation;[12] however, similar results were found and no dependence of χ^2 on the distance parameter, r, was found, suggesting that the Debye–Hückel limiting law was sufficient for the description of the experiments. Thus, the simpler approach was chosen. Association constants for $[OsCp_2I]CF_3SO_3$ are given in Table II.

Supplementary material tables contain the NMR data, including experimental conditions of solvent, temperature, and reactant concentrations, for each experiment. Also included are the overall rate constants calculated for each sample, on the basis of a second-order rate law and modified Bloch equations as presented in refs 2 and 11. Further, tables of the conductivity data are given.

Discussion

The results will be discussed separately for the higher dielectric constant solvents, dimethyl sulfoxide, acetonitrile, nitromethane, nitrobenzene, and acetone, and the more complex situation of the low dielectric solvents, methylene chloride, tetrahydrofuran, bromobenzene, and chloroform.

Considering first the higher dielectric constant solvents, the exchange rate constants in acetonitrile, nitromethane, and nitrobenzene are 42, 61, and 8, respectively, times slower for the $OsCp_2/OsCp_2I^+$ reactions than for the analogous Ru ones. Compared to the $RuCp_2/RuCp_2Br^+$ system, the Os reaction is 11, 13, and 11 times faster in acetonitrile, nitromethane, and nitrobenzene. Thus, the rate constants for the $OsCp_2/OsCp_2I^+$ reaction are significantly lower than those of the analogous Ru reaction and higher than those of the $RuCp_2/RuCp_2Br^+$ reaction. The variation with solvent is similar to that of the latter reaction. In the present study the range of solvents has been extended to include dimethyl sulfoxide and acetone, with higher and lower dielectric constants than the others in this class. They also gave the most extreme rate constants with the lowest value occurring in dimethyl sulfoxide and the highest in acetone, giving an overall solvent effect range in the polar solvents of a factor of 22. This is a high sensitivity compared to the other systems that have been studied, such as metallocene electron-self-exchange reactions.[13]

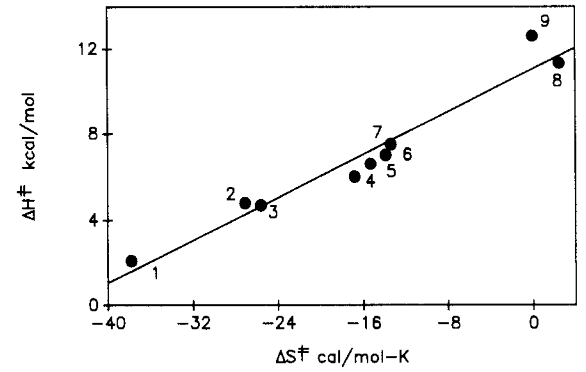

Figure 3. Plot of activation enthalpy vs activation entropy: (1) tetrahydrofuran; (2) chloroform; (3) bromobenzene; (4) methylene chloride; (5) nitrobenzene; (6) nitromethane; (7) acetonitrile; (8) acetone; (9) dimethyl sulfoxide.

Recent studies of the electron/atom exchange between $CpM(CO)_3^-$ and $CpM(CO)_3X$ (M = Mo, W; X = Cl, Br, I)[3] and between $CpM(CO)_3^-$ and $CpM(CO)_3H$ (M = Cr, Mo, W)[4] also show that the exchange rate constant for the second transition series centers (Ru, Mo) are higher than for the third transition series metal center (Os, W). Since the metal–halogen or metal–hydrogen bond has to be broken at some stage, the pattern may be due to the greater bond strength for the third transition series metal. A possibly related observation is that $OsCp_2I^+$ shows much less tendency to decompose in strong donor solvents, such as acetone, dimethyl sulfoxide, and tetrahydrofuran, than the Ru analogue. With regard to the halogen, the reactivity pattern found for the Os system is the same as for the Ru systems and for the Mo and W systems mentioned above. The observed rate constants, to the extent that they can be measured, increase in the order Cl < Br < I, the order expected on the basis of the decreasing M–X bond strength. Quantitatively, however, there is some difference. For the $OsCp_2/OsCp_2Br^+$ reaction, an estimated rate constant of 3 M^{-1} s^{-1} at 90 °C in acetonitrile has been reported,[5] which is slower by a factor of over 6000 compared to that of the $OsCp_2/OsCp_2I^+$ reaction. For the Ru systems, the analogous factor is 100–800, depending on the solvent, while for the $CpM(CO)_3^-/CpM(CO)_3X$ reactions it is 1100–1600.

The activation parameters for the reaction studied here vary a great deal with solvent and in a compensating manner, as shown in Figure 3. This compensation minimizes the variation of the rate constant for such a large variation in enthalpy and entropy of activation. Considering the higher dielectric constant solvents, ΔH^* has a maximum of 12.6 kcal/mol and ΔS^* is 0 for dimethyl sulfoxide, while for nitrobenzene ΔH^* is 6.6 kcal/mol and ΔS^* is −15 cal/(mol K). This trend of a decreasing enthalpy of activation accompanied by a more negative entropy of activation continues in the low dielectric constant solvents. The most extreme case is tetrahydrofuran, for which ΔH^* is only 2.2 kcal/mol and ΔS^* is −38 cal/(mol K). A similar extent and pattern of compensation as a function of solvent was observed for the $RuCp_2/RuCp_2I^+$ but not the $RuCp_2/RuCp_2Br^+$ reaction. We thus conclude that the presence of the iodide makes the reaction especially solvent sensitive. The compensation behavior can be taken as evidence of a common mechanism or a smooth variation between similar mechanisms. However, it makes it difficult to interpret the activation parameters in terms of contributions from metal–halogen bond breaking. If we take the trend in the activation parameters as primarily reflecting the solvent reorganization or displacement required to form a transition state, then the pattern might be rationalized as follows. The interaction between the

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Table III. Parallel First- and Second-Order Analysis of $MCp_2/[MCp_2I]CF_3SO_3$ Exchange Reactions

metal	solvent	T, °C	$10^{-3}k_1$, $M^{-1}\ s^{-1}$	k_2, s^{-1}
Os	CD_2Cl_2	20	29 ± 2	130 ± 10
	$CDCl_3$	20	1.0 ± 0.1	2.7 ± 0.4
Ru	CD_2Cl_2	-50	18 ± 2	50 ± 20
	$CDCl_3$	20	7.9 ± 0.3	8 ± 2
	$CDCl_3$	-20	4.2 ± 0.7	6 ± 4
	CD_3CN	-30	54 ± 1	6 ± 1

MCp_2 center and the X group on MCp_2X^- should have a small, negative ΔH^* and a negative ΔS^*, as well as a negative ΔV^*. However, to the extent that solvent must be displaced and restructured between the reactants, there will be a positive contribution to ΔH^* and a positive contribution to ΔS^* as well as ΔV^*. The more strongly solvated the reactants, and in particular the halogen, the larger will be the solvent contribution. The strength of solvation apparently follows closely the dielectric constant, such that the solvation contribution dominates in the higher dielectric constant solvents.

As shown in Figure 2, the lower dielectric constant, halogenated solvents methylene chloride and chloroform, do not strictly follow a second-order rate law. Instead there is an increase in the apparent second-order rate constant at low concentrations of Os(IV). Similar behavior was observed previously for the $RuCp_2/RuCp_2Br^+$ reaction, and it was attributed to a strong influence of ion pairing on the bimolecular process. The data on the Os system are not fit by such a rate law because it cannot describe the large increase in rate at low [Os(IV)]. An alternative that fits both the previous and the current results involves a two-term rate law. One term is first-order in each of the reactants and the other is pseudo first order in [Os(II)] or [Ru(II)] and independent of [Os(IV)] or [Ru(IV)]

$$\text{rate} = k_1[\text{M(II)}][\text{Os(IV)}] + k_2[\text{M(II)}]$$

For such a rate law, a plot of the rate/[Os(II)] vs [Os(IV)] (apparent second-order rate constant times [Os(IV)]) should be linear with a slope of k_1 and an intercept of k_2. Such a treatment is presented in Figure 4, and it describes the data. The parameters derived are given in Table III. The data from the Ru system in some solvents are less precise than the Os data, but the scatter about the line is not systematic. The mechanistic nature of the k_2 path presumably involves the steady-state formation of a small amount of a reactive form of Os(II) or Ru(II). This may involve specific interaction with the solvent to open the space between the Cp rings in order to facilitate interaction with the halogen. This interaction might be related to the formation of charge-transfer complexes between metallocenes and chloromethanes.[14] We saw no evidence for any isomerization processes of the $OsCp_2$. Further work will be to look at other characteristics of this path, and attempts will be made to look at other reactions of $OsCp_2$ or $RuCp_2$ that might show the same limiting rate constants. From the data on the $RuCp_2/RuCp_2I^+$ reaction in chloroform at 20 and -20 °C, estimates of the enthalpy and entropy of activation for the k_1 path are 1.8 kcal/mol and -35 cal/(mol K). The values of k_2 are not well enough defined to justify any calculation, but the enthalpy of activation is apparently quite low. Values of 1.9 kcal/mol for ΔH^* and -34 cal/(mol K) for ΔS^* are obtained, if the data are assumed to be strictly second order, by using 48 data points in the range -60 to 30 °C and Ru(II) concentrations of 8.5 and 9.1 mM, with 5.4 and 6.5 mM Ru(IV), respectively. If this estimate for the second-order term in the parallel path treatment is representative, then the activation parameters obtained by assuming a simple bimolecular rate law should be approximately correct. Furthermore, if the Os(IV) or Ru(IV) concentration is above about 4 mM, then the bimolecular path will be dominant and direct comparison to the results for the higher dielectric constant solvents is strictly justified.

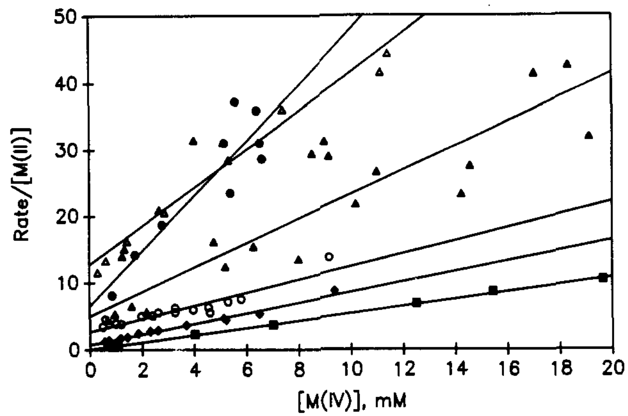

Figure 4. Test of the rate law with parallel first- and second-order paths. The rate divided by the total M(II) concentration, equal to the apparent-second order rate constant times [M(IV)], is plotted vs the total M(IV) concentration. The symbols and multipliers are as in Figure 2.

The consideration of the additional first-order path in chloroform and methylene chloride prompts an analogous analysis of the higher dielectric constant solvent data for which concentration dependence data were acquired. The most detailed data set available[2] is for $RuCp_2/RuCp_2I^+$ in acetonitrile at -30 °C with 19.7–0.85 mM $RuCp_2I^+$ and 1.81–14.0 mM $RuCp_2$. Reanalysis of these data gives a k_1 value of $5.4 \pm 0.1 \times 10^4\ M^{-1}\ s^{-1}$ and a k_2 value of $3 \pm 2\ s^{-1}$. The previously quoted value, assuming a simple second-order rate law, was $5.5 \pm 0.2 \times 10^4\ M^{-1}\ s^{-1}$. Thus, the k_2 path is only marginally apparent and negligible at the high concentration of $RuCp_2I^+$, 9.1 mM, used for the temperature-dependence study.

We must still consider that in the lower dielectric constant solvents, chloroform, methylene chloride, bromobenzene, and tetrahydrofuran, ion pairing is essentially complete under the experimental conditions. According to the two-term rate law, only the k_1 path should be influenced by ion pairing, and it is this path that should be compared to the single path observed in the higher dielectric constant solvents. The rate constant for the k_1 path in methylene choride is comparable to that in nitromethane and nitrobenzene. Chloroform gives a much lower rate constant. Ion pairing alone cannot be the difference between these two cases, and the other relatively low rate constants are for dimethyl sulfoxide as well as bromobenzene and tetrahydrofuran. Some strong and specific solvent interactions are apparently involved.

These reactions are intriguing because they involve what is formally both electron and atom transfer, or X^+ transfer, and can be compared to substitution processes. Although it seems most likely that a bridged mechanism is involved in the detailed mechanism, the experimental data do not yet allow a more detailed description of the process. A variety of closely related options have been considered by Taube[5] and by Creutz.[3] Extension of this work and detailed analysis of related reactions that are being developed should allow more definitive mechanistic interpretation. Further work in our laboratory is planned on the slower reactions involving Cl and Br compounds, as well as ΔV^* measurements on the reactions reported here.

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Supplementary Material Available: Tables 1–16, listing observed second-order rate constants as a function of temperature and solvent and conductance data for $[OsCp_2I]CF_3SO_3$, $[RuCp_2Br]PF_6$, and $[RuCp_2I]CF_3SO_3$ in chloroform and methylene chloride at various temperatures (12 pages). Ordering information is given on any current masthead page.

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