Halogen-Mediated Electron Transfer between Metallocenes of Ruthenium and Osmium in the Oxidation States 4+ and 2+

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The rates of self-exchange for several systems of the class MCp_2X^+/Cp_2, where M is Ru or Os and X is Cl, Br, or I, have been measured by the NMR line-broadening method. For each metal, the rates increase along the halogen series as given above and are more rapid for M = Ru than for the osmium analogues. In consideration of these data, the possibility is raised that these 2e self-exchange reactions and those of other metal ions take place by 1e steps.

Introduction

The advantages of substitution-inert metal complexes in the study of the mechanisms of electron-transfer reactions are widely appreciated. An abundant literature on 1e changes in which such species are featured has been generated. This stands in marked contrast to the situation for 2e changes, where the literature is very sparse. The most extensive studies on 2e changes have been carried out on the reactions of complexes of Pt(II) with Pt(IV)[1–3] involving "atom" transfer from the oxidant to the reductant. For the purposes of reaching an understanding of the phenomena at a basic level, simplicity is desirable. In this respect, the Pt(II)–Pt(IV) systems fall short of the ideal because two ligands must be added to the Pt(II) species in oxidizing it to Pt(IV). The observations made on the reactions show that one of these ligands is derived from the oxidant ("atom" transfer) and the second is gathered from the environment. In most of the cases thus far studied, the latter is a solute species, and because the affinity of Pt(II) for a fifth ligand such as Cl^- is low, third-order rate laws are registered. In the course of our studies on the dicyclopentadienide complexes of Ru(IV) and Os(IV) we have encountered a class of 2e changes of very simple chemistry, e.g.

$$MCp_2X^+ + MCp_2 = MCp_2 + MCp_2X^+$$
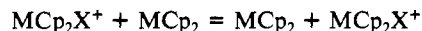
where X = Cl, Br, or I.

The rates of most of the self-exchange reactions are in a range that makes them accessible by the NMR line-broadening technique. The cross reactions, oxidation of $OsCp_2$ by $RuCp_2X^+$, are rapid, but those with X = Cl or Br are slow enough so that the rates proved to be measurable by stopped-flow methods.

Experimental Section

Materials. Ruthenocene and osmocene were obtained from Strem Chemical, Inc. The NMR solvents, CD_3CN and CD_3NO_2, were obtained from Merck Sharp and Dohme Canada, Ltd., Sigma Chemical, or Cambridge Chemical. These solvents were used as obtained in sealed ampules. The nitromethane used in the stopped-flow experiments was purified by literature methods.[4] The compounds $[RuCp_2Cl]PF_6$ and the bromo analogue were prepared as previously described.[5] This procedure proved unsatisfactory for X = I. In the method we followed, $[RuCp_2I]I_3$, prepared by an established method,[6] was the starting material. To prepare a salt with an indifferent anion, 1.0 g of $[RuCp_2I]I_3$ dissolved in 100 mL of purified nitromethane was titrated over a period of 0.5 h with a nitromethane solution (100 mL) containing 0.35 g of either $AgPF_6$ or $AgCF_3SO_3$ (for the $CF_3SO_3^-$ salt). The mixture was allowed to stir for an additional 1 h, whereupon AgI was removed by filtration. The filtrate was rotavaporated to dryness. To remove residual I_2, the solid was repeatedly extracted with portions of CCl_4 until the extract was almost colorless. The solid was then washed with ether and dried. This material

was crystallized twice from hot dichloromethane/heptane. It is important to filter the solution before adding heptane so as to remove any of the unconverted triiodide salt. The osmium analogue was prepared in a similar manner by starting with $[OsCp_2I]I_3$.[7]

To prepare $[OsCp_2Cl]PF_6$, osmocene (0.50 g) was dissolved in 50 mL of benzene, this solution being added to 25 mL of 4 M HCl containing 4.0 g of $FeCl_3 \cdot H_2O$. The two-phase mixture was stirred vigorously for 18 h. The acid layer was collected and washed with aliquots of benzene and then ether. An aqueous solution containing 2.0 g of NH_4PF_6 was added, resulting in the immediate formation of a crystalline material. This was collected, dried, and recrystallized from dichloromethane/heptane. The yield was ca. 80%.

A similar procedure was followed for $[OsCp_2Br](PF_6)$ with the exception that the oxidant was $FeNH_4(SO_4)_2 \cdot 12H_2O$ in 3 M HBr. The yield was ca. 85%.

The complex $RuCp*_2Br^+$ ($Cp*$ represents permethylated cyclpentadienide ion) was needed for some experiments, and the hexafluorophosphate salt was prepared by the following procedure. Permethylated ruthenocene (100 mg) dissolved in 20 mL of CH_2Cl_2 was added to 110 mg of $RuCp_2BrPF_6$ dissolved in 150 mL of CH_2Cl_2. The reaction mixture was stirred for 15 min and the solvent removed. $RuCp_2$ and excess $RuCp_2*$ were extracted with ether. The remaining solid was crystallized twice from CH_2Cl_2/C_7H_{16}. Anal. Calcd for $C_{20}H_{30}RuBrPF_6$: C, 40.28, H, 5.07; Br, 13.40; P, 5.19. Found: C, 40.28; H, 5.06; Br, 13.65; P, 5.30.

NMR Experiments. The NMR spectra were recorded on a Varian XL-100 spectrometer. The chemical shifts were determined with Me_4Si as a reference. The chemical shift values, δ, used in the line-shape calculations for CD_3NO_2 solutions were measured as follows: $RuCp_2$ (4.53), $[RuCp_2X]PF_6$ (6.08 ± 0.01), $OsCp_2$ (4.71), $[OsCp_2I]PF_6$ (6.06), $[OsCp_2Br]PF_6$ (5.97). For the self-exchange in CD_3CN, values of δ 4.52 and 6.07 were measured for $RuCp_2$ and $[RuCp_2I]PF_6$, respectively. The temperatures, below 30 °C, were determined by using the chemical shift difference between the five signals in neat methanol. For above-ambient temperatures, a thermometer was inserted into the probe.

Appropriate quantities of the metallocenes and halometallocene complexes were placed in a volumetric flask and diluted to the mark with the desired deuteriated solvent. The solutions were stable for weeks if sealed with Parafilm and stored in a freezer. Initial rates were obtained by fitting digitized spectra using a modification of the program given by Sandstrom.[8] These rates were used as a starting point to generate a family of spectra. The rate constants giving the best visual fit are recorded in the tables. The natural line widths of the individual components are 1.0 ± 0.5 Hz, and the variation with temperature was found to be negligible. The errors for the activation parameters were estimated by a graphical method, allowing for a 10% error in the rate constants and a variation of 2 °C in temperatures. For the self-exchange reactions of $OsCp_2Br^+/OsCp_2$ and $RuCp_2Cl^+/RuCp_2$ the errors are larger, the broadening due to exchange being quite small.

Stopped-Flow Experiment. Stopped-flow experiments were done on an Aminco Morrow apparatus equipped with an oscilloscope. The temperature was determined by a thermocouple attached to the block. The block was allowed to equilibrate for 20 min at the chosen temperature. The nitromethane was purified immediately before use. Solutions of the halometallocenes were wrapped in aluminum foil to exclude light. The course of the reaction was followed by a decrease in absorbance in the region between 410 and 450 nm, which is associated with the disappearance of the ruthenium(IV) species. To ensure pseudo-first-order conditions, the concentration of $OsCp_2$ was kept a factor of at least 10

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Table I. $[RuCp_2I]PF_6$ (3 mM)/$RuCp_2$ (3 mM) in CD_3NO_2

T, K	$10^{-5}k_2$, M^{-1} s^{-1}	T, K	$10^{-5}k_2$, M^{-1} s^{-1}
246	0.81	272	5.6
251	1.2	285	11
256	1.6	292	13
365	3.3	300	21

Table II. $[RuCp_2I]CF_3SO_3$ (3 mM)/$RuCp_2$ (3 mM) in CD_3CN

T, K	$10^{-4}k_2$, M^{-1} s^{-1}	T, K	$10^{-4}k_2$, M^{-1} s^{-1}
242	9.3	273	41
250	9.7	288	52
265	26	299	69

Table III. $[RuCp_2Br]PF_6$ (30 mM)/$RuCp_2$ (30 mM) in CD_3NO_2

T, K	$10^{-3}k_2$, s^{-1}	T, K	$10^{-3}k_2$, s^{-1}
304	3.3	344	24
328	12	357	40
330	12	363	47
335	16	366	63

Table IV. $[OsCp_2I]PF_6$ (3 mL)/$OsCp_2$ (3 mM) in CD_3NO_2

T, K	$10^{-5}k_2$, M^{-1} s^{-1}	T, K	$10^{-5}k_2$, M^{-1} s^{-1}
275	0.20	334	2.40
286	0.39	342	3.30
306	0.86	359	6.70
321	1.50	369	10.0

Table V. $[RuCp_2Cl]PF_6$ (1.74 mM)/$OsCp_2$ (4.7 mM) in CH_3NO_2

T, K	$10^{-2}k_2$, M^{-1} s^{-1}	T, K	$10^{-2}k_2$, M^{-1} s^{-1}
254	0.73	300	1.85
259	1.00	304	2.4
294	1.40	309	2.5

Table VI. Activation Parameters

system	solvent	ΔH^{*}, kcal mol^{-1}	ΔS^{*}, cal mol^{-1} deg^{-1}
1. $[RuCp_2I]CF_3SO_3/RuCp_2$	CD_3CN	5.4 ± 1.3	−13 ± 5
2. $[RuCp_2I]PF_6/RuCp_2$	CD_3NO_2	8.3 ± 0.8	−2 ± 3
3. $[RuCp_2Br]PF_6/RuCp_2$	CD_3NO_2	9.3 ± 1.1	−12 ± 4
4. $[RuCp_2Cl]PF_6/OsCp_2$	CH_3NO_2	9.0 ± 2	−18 ± 6
5. $[OsCp_2I]PF_6/OsCp_2$	CD_3NO_2	7.5 ± 1	−12 ± 2

greater than that of the $RuCp_2X^+$ species. The reactions were shown by NMR spectroscopy to be complete under the experimental conditions.

The uncertainty in reaction temperature is ±1°. The uncertainty in rate constants for the reaction with $RuCp_2Cl^+$ as oxidizing agent is ±5% but is ±30% for the experiment with the bromo analogue as oxidant.

Determination of the Equilibrium Constant for the $RuCp^*_2Br^+/OsCp_2$ System. A sample of $OsCp_2$ (0.0084 g, 0.026 mM) was dissolved in 1.5 mL of CD_3NO_2 in a 2.0-mL volumetric flask. A sample of $[RuCp^*_2Br]PF_6$ (0.0052 g, 0.009 mM) was then dissolved in the $OsCp_2$ solution, and more CD_3NO_2 was added to fill the volumetric flask to the mark. After thorough mixing, a 1-mL sample was removed and loaded into a NMR tube. The tube was sealed and stored in the dark at 22 °C. Successive ^1H NMR spectra were registered until no further change was observed (ca. 4 days), and the equilibrium concentrations were calculated by integrating the signals for the various species: $OsCp_2Br^+$ (5.97 ppm); $OsCp_2$ (4.71 ppm); $RuCp^*_2Br^+$ (1.92 ppm); $RuCp^*_2$ (1.65 ppm).

Results

The room-temperature 100-MHz proton NMR spectrum of a solution 3.0×10^{-3} M in $RuCp_2$ and in $[RuCp_2I]PF_6$, with CD_3NO_2 as solvent, exhibits a single resonance at δ 5.23. As the solution is cooled, the peak broadens and eventually resolves into two peaks at δ 4.53 and 6.08. These peak positions correspond to those observed for separate CD_3NO_2 solutions of $RuCp_2$ and $[RuCp_2I]PF_6$, respectively. The coalescence temperature is −23 ± 2 °C. The second-order rate constants were calculated by total line-shape analysis, and the values are listed in Table I. For a solution in CD_3CN, 3.0×10^{-3} M in both $RuCp_2$ and $[RuCp_2I]CF_3SO_3$, the coalescence temperature was found to be −22 ± 2 °C. The rate constants calculated as outlined above are recorded in Table II. It is to be noted that over the same temperature range the rate constants when PF_6^- is the counterion change by a factor of ca. 25, while with CF_3SO_3 as counterion, the factor is only 8. Thus the near-identity of the coalescence temperatures as reported is fortuitous. For $RuCp_2/[RuCp_2I]PF_6$ in CD_3CN and $RuCp_2/[RuCp_2I]CF_3SO_3$ in CD_3NO_2 they are −2 ± 1 and 37 ± 2 °C.

For $RuCp_2/[RuCp_2I]CF_3SO_3$ in CD_3CN, the rate was studied as a function of concentration, with the total concentration of Ru kept at the 6.0 mM level but with the concentration ratios at 1/3, 1/1, and 3/1. In this series, an average value of $k = (1.9 \pm 0.3) \times 10^5$ M^{-1} s^{-1} at −17 °C was observed, which can be compared to 1.8×10^5 M^{-1} s^{-1} interpolated from the data in Table II.

In contrast to the case for the iodo system, $RuCp_2/[RuCp_2Br]PF_6$ in CD_3NO_2 gives rise to two resolved (though slightly broadened) peaks at room temperature. The rate was studied as a function of temperature for a solution in CD_3NO_2, 30 mM in each reagent, and the resulting data are shown in Table III. With the corresponding chloro system the rate is so slow that only a rough estimate of the rate could be obtained even at 93 °C: $k \approx 7$ M^{-1} s^{-1}, where the rate may be in error by a factor of 2. Decomposition at higher temperatures precluded extending the temperature range.

The osmium self-exchange reactions are slower than those for the corresponding ruthenium couples. For them, it was possible to obtain data of reasonable quality only for X = I; these are summarized in Table IV. For X = Br, we encountered difficulties similar to those described for the slowest ruthenium system; k is estimated as 3 M^{-1} s^{-1} at 90 °C for the PF_6 salt in CD_3CN, the error in the measurement again amounting to a factor of 2. For X = Cl, the rate is beyond the scope of the NMR method.

The ruthenium couples are more strongly oxidizing than the corresponding osmium couples, and reactions of Ru(IV) with Os(II) are so complete that there seems to be no easy way of obtaining the equilibrium quotients. The reaction with X = I is too rapid for our stopped-flow equipment, and even that with X = Br is so rapid that good data were not obtainable. For the latter reaction we report $k = (5 \pm 2) \times 10^4$ M^{-1} s^{-1} at 30 °C in CH_3NO_2. The reaction with X = Cl was studied in more detail, and the results of this effort, which established the reaction as first order in each reagent, are summarized in Table V.

The equilibrium quotient for reaction 1 was determined as (6 ± 2) × 10^{-2} at 22 °C (in CD_3NO_2 with PF_6^- as the counterion).

$$RuCp^*_2Br^+ + OsCp_2 = RuCp^*_2 + OsCp_2Br^+ \qquad (1)$$

This shows the $OsCp_2Br^+/OsCp_2$ couple to be more strongly oxidizing than $RuCp^*_2Br^+/RuCp^{*+}$ by 0.036 V. The indications are that the kinetics of the reaction do not conform to expectations for a simple second-order process (with proper allowance being made for the reaction being incomplete).

Discussion

The salient results emerging from this study are (a) the rates of the self-exchange reactions decrease in the order I$^-$ > Br$^-$ > Cl$^-$ and (b) the rates of self-exchange are greater for ruthenium systems than they are for the analogous osmium systems.

The reactivity order noted under (a) is that observed for the Pt(IV)/Pt(II) systems, if it can be assumed that the complication of adding a sixth ligand to Pt(II) as reactant is not controlling. This relative order, though not invariably, is frequently enough observed so that it has been called "normal".

As to (b), it provides the first comparison that can be made for simple 2e atom transfers between closely related metal centers and thus there is no previous experience on which a prediction might have been based, nor are the issues well enough understood so that the outcome could have been foreseen on theoretical grounds. In the following we point to some of the issues that come to mind in trying to understand the observations.

One explanation of the "normal" order is that electron delocalization in the activated complex, here assumed to be symmetrical, is great and that there is a strong admixture of the state $Ru^{III}XRu^{II}$ into the ground state $Ru^{IV}X^-Ru^{II}$. If the resulting stabilization materially decreases the activation energy, the order

is at once accounted for. An extreme extension of this view is to attribute the highest reactivity to the iodo complex because it can reasonably be supposed that breaking the metal–ligand bond would be easiest for X = I, at least if this is done homolytically. This view, however, is incomplete because it makes no allowance for bond making in the activated complex.

An additional issue needs to be addressed in considering the activation process for the 2e change: in the activated condition in which the system is structurally symmetrical (hereinafter referred to as the isoergic condition), how does the state $M^{IV}\cdot X^-\cdot M^{II}$ compare in energy to the state $M^{III}\cdot X^-\cdot M^{III}$? If the latter lies lower, then, even in a net 2e-transfer reaction, electron transfer would take place by successive 1e steps.

This is a point that must be considered seriously for transition-metal ions. The standard free energy changes in the gas phase for reactions of the type

$$M^{4+} + M^{2+} = 2M^{3+} \qquad (2)$$
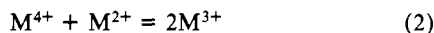
can be calculated from the ionization potentials for the processes $M^{2+} = M^{3+} + e^-$ and $M^{3+} = M^{4+} + e^-$. Unfortunately, they are not available for the systems of present interest. They are tabulated for V, Cr, Mn, Fe, Co, and Mo, and the values of $-\Delta G°$ (10^2 kcal) for these elements are 4.0, 4.2, 6.4, 5.6, 4.1, 4.4, respectively.[9] The interaction of $M^{4+} + M^{2+}$ on the one hand and $2M^{3+}$ on the other with the environment will to some extent compensate for the instability of the heterovalent state in the gas phase. If the states are treated as intermediates and, for the case of liquid water as the environment, the interaction with the solvents is treated as being proportional to Z^2/r (where Z and r are ionic charge and radius, respectively), the stabilization of the heterovalent state relative to the isovalent amounts to twice the hydration free energy of a monodipositive ion of the radius of the metal ion in the isoergic condition. For Li^+, with a radius of 0.60 Å, smaller than the radius in question, $-\Delta G°$ for hydration is 1.22×10^2 kcal,[10] and twice this falls far short of making up for the energy defect for reaction 2 in the gas phase.

In the above, the interactions of the ions with the environment are dealt with in a highly idealized and therefore unrealistic way. It is therefore pertinent to note the high stability of the isovalent state in the gas phase proves to be the dominant factor also in governing the equilibrium behavior, at least in acidic solution and in the cases where data is available for mononuclear species; for all of the transition metals mentioned the intermediate oxidation condition is stable with respect to the extremes in the equilibrium sense. In the reactions of the heterovalent species with each other, in passing through the intermediate isoergic condition, the heterovalent state will lose stabilization by the environment, relative to that for the isovalent state.

General experience teaches that in normal coordination environments, comproportionation of Os(IV) + Os(II) to Os(III) is less favorable than the corresponding reaction for Ru. If in fact the self-exchange reactions proceed by 1e steps, and if the general statement about relative stabilizies applies to the activated complex, the slower self-exchange rate for the Os(IV)/Os(II) couple is accounted for qualitatively.

Regardless of whether the reactions proceed by a concerted 2e change or in a stepwise fashion, an important consideration is the inner-sphere barrier to electron transfer. The relevant structural data do exist for $RuCp_2$ and $RuCp_2I^+$.[11,12] The M–C distances

are found to be the same within 0.01 Å; the C–C distances are the same within 0.02 Å. The chief structural distortion on oxidation is the change in dihedral angle by 32.2° and, of course, the placement of the halide ion. Thus the reaction coordination involves mainly ring tilting and relocation of the bridging group in the activated complex. The activation energies (Table VI) are observed to be low, but in view of the dependence of the activation parameters on the nature of the counterion and of the solvent, detailed discussion of our rather sparse data seems unwarranted.

In each case the cross reactions are more rapid than are either of the corresponding self-exchange reactions. In terms of the Marcus–Hush correlation, this is attributable to there being a substantial driving force for the cross reactions. When the correlation is applied to the data for the oxidation of $OsCp_2$ by $[RuCp_2Br]PF_6$, the only case where the necessary data are in hand, K_{eq} is calculated as 3×10^4 at 30 °C. This corresponds to $E°$ for the Ru(IV)/Ru(II) couple being ca. 131 mV more oxidizing than that for the corresponding osmium couple.

Because of the irreversibility of the $M^{IV}Cp_2/M^{II}Cp_2$ couples, the equilibrium quotients for the cross reactions are not obtainable from electrochemical data. Exploratory experiments showed that the equilibrium quotient for the $[RuCp_2Br]PF_6/OsCp_2$ reaction must be greater than 3×10^4 and moreover that it could be obtained for reaction 1 (that is, with $RuCp^*_2$ replacing $RuCp_2$). As reported in the Results, $nE°$ for reaction 1 is −0.072 V. We attempt to set a limit of $nE°$ for $RuCp_2Br^+/RuCp_2 + Br^-$ in the following way. We assume that $RuCp_2^+/RuCp_2$ is more oxidizing than $RuCp_2^+/RuCp^*_2$ by the amount 0.52 V, determined by the analogous iron couples.[13] The next stage, Ru(IV)/Ru(III), is more difficult to deal with. The species $RuCp_2^+$ is surely more difficult to oxidize than is $RuCp^*_2^+$, but in this step there is compensation because the affinity of $RuCp_2^{2+}$ for Br^- is expected to be greater than that of $RuCp^*_2^{2+}$. We assume that the difference in affinity for Br^- will not fully compensate for the difference in the work of removing the electron and thus find that $nE°$ for
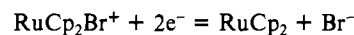
$$RuCp_2Br^+ + 2e^- = RuCp_2 + Br^-$$

is greater than 0.52 V or that $E°$ for the $RuCp_2Br^+/RuCp_2$ couple exceeds that of the corresponding osmium couple by more than 0.23 V (>(0.52 − 0.07)/2).

In view of the uncertainty of the assumptions made in estimating, the disparity of 131 mV arrived at by recourse to the Marcus–Hush correlation is not great enough to disquality the correlation as applying to 2e redox processes. It needs, however, to be point out that even if the self-exchange reactions proceed in 1e steps, a change in mechanism to the 2e pathway is expected when the driving force for the cross reaction becomes large. In these circumstances the activated complex for the 2e change has much the character of the reactants, and the probability that the energy of the activated complex for the 1e path will be below that for the 2e path and above that of the reactants is much reduced.

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