transfer mechanism for this class of pentacoordinate compounds. Available data now suggest that there may exist a relationship between the rate of intramolecular conformational mobility in the Cu(I) compounds and the rate of electron self-exchange between the Cu(I/II) pairs. Finally, the study of the self-exchange rate constant for $[\mathrm{Cu^{I,II}}((5\text{-MeimidH})_2\mathrm{DAP})]^{+/2+}$ as a function of temperature is the first such study for these pentacoordinate complexes. The activation parameters indicate that the relatively large self-exchange rate constant ($k'_{44} = 3.5 \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$ at 293 K) is dominated by an unusually favorable ΔH^{*} (16 kJ $\mathrm{mol^{-1}}$) contribution.

Acknowledgment. At Rice University, this work was supported by National Institutes of Health Grant GM-28451 from The National Institute of General Medical Science and Grant C-624 from The Robert A. Welch Foundation. Work at the University of Notre Dame was supported by National Institutes of Health Grant GM-38401. The Rigaku AFC-5S X-ray diffractometer, at Rice, was purchased, in part, through an instrumentation grant from The National Science Foundation.

Supplementary Material Available: Tables S-II, S-IV, and S-V, listing final anisotropic thermal parameters, fixed hydrogen atom coordinates, and rigid group parameters, respectively, for $[\mathrm{Cu^{II}}((\mathrm{imidH})_2\mathrm{DAP})](\mathrm{BF_4})_2$, and Table S-VI, listing the calculated least-squares planes (6 pages); Tables S-I and S-III, listing observed and calculated structure amplitudes (×10) for $[\mathrm{Cu^{II}}((5\text{-MeimidH})_2\mathrm{DAP})](\mathrm{BF_4})_2\cdot{}^1/_2\mathrm{CH_3OH}$ and $[\mathrm{Cu^{II}}((\mathrm{imidH})_2\mathrm{DAP})](\mathrm{BF_4})_2$ (30 pages). Ordering information is given on any current masthead page.

Contribution from Ames Laboratory and the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Oxidative Homolysis of Organochromium Macrocycles

Carl R. Steffan, James H. Espenson,* and Andreja Bakac*

Received August 24, 1990

The complexes $\mathrm{RCrL(H_2O)^{2+}}$ (R = alkyl, aralkyl; L = 1,4,8,12-tetraazacyclopentadecane) are oxidized by $\mathrm{Ru(bpy)_3^{3+}}$ and $^2\mathrm{E}$ $\mathrm{Cr(bpy)_3^{3+}}$. The one-electron oxidized species $\mathrm{RCrL(H_2O)^{3+}}$ undergoes subsequent homolysis; the $\mathrm{R^{\bullet}}$ radicals so produced may react with certain metal complexes, or they dimerize, depending on conditions. The rate constants for the rate-controlling step, electron transfer from $\mathrm{RCrL(H_2O)^{2+}}$ to $\mathrm{Ru(bpy)_3^{3+}}$ or $\mathrm{{}^*Cr(bpy)_3^{3+}}$, were measured by laser flash photolysis for an extensive range of R groups. For $\mathrm{Ru(bpy)_3^{3+}}$, the rate constants range from 14.2 L $\mathrm{mol^{-1}\ s^{-1}}$ ($\mathrm{R = CH_3}$) to 1.05×10^9 ($\mathrm{R = 4\text{-}CH_3C_6H_4CH_2}$); for $\mathrm{{}^*Cr(bpy)_3^{3+}}$, the corresponding values are 2.8×10^6 and 1.55×10^9 L $\mathrm{mol^{-1}\ s^{-1}}$. In both series, the order of rate constants is methyl < primary alkyl < secondary alkyl < aralkyl. The plots of log *k* versus the gas-phase ionization potentials of $\mathrm{R^{\bullet}}$ are linear, in accord with the rate-controlling step being electron transfer.

Introduction

One-electron oxidation of an organometal ($\mathrm{L_nMR}$) leads to an oxidized species ($\mathrm{L_nMR^+}$) whose fate is often but not always homolysis ($\rightarrow \mathrm{L_nM^+ + R^{\bullet}}$). This process, collectively termed oxidative homolysis, has been examined for a considerable number of organometals. This includes the oxidation of $\mathrm{R_4Pb}$ ($\mathrm{R = CH_3, C_2H_5}$)[1,2] and $\mathrm{R_2Hg}$[3] by $\mathrm{IrCl_6^{2-}}$, oxidative coupling of $\mathrm{R_2Fe(bpy)_2}$[4,5] and $\mathrm{R_2Ni(bpy)}$[4] and oxidation of $\mathrm{R_4Sn}$[6-8] and $\mathrm{R_2Pt(PPh_3)_2}$.[9] Considerable effort has also been devoted to the oxidation of $\mathrm{RCo(dmgH)_2H_2O}$ and its numerous Schiff-base analogues.[10-30]

The present study arises from previous work dealing with the oxidation of $\mathrm{(H_2O)_5CrR^{2+}}$ and $\mathrm{RCrL(H_2O)^{2+}}$ (L = 1,4,8,12-tetraazacyclopentadecane) complexes.[31-35] In the pentaaqua series, oxidants include $\mathrm{Ni([14]aneN_4)^{3+}}$, $\mathrm{Ru(bpy)_3^{3+}}$, $\mathrm{NO^+}$, and

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$^*Cr(bpy)_3^{3+}$, whereas for the macrocyclic series only $IrCl_6^{2-}$ and $ABTS^{\bullet-}$ have been examined ($ABTS^{2-}$ = 2,2'-azinobis(3-ethylbenzthiazoline-6-sulfonate). We decided to undertake a systematic study of the oxidation of an extensive series of $RCrL(H_2O)^{2+}$ complexes by $Ru(bpy)_3^{3+}$ and $^*Cr(bpy)_3^{3+}$, eqs 1 and 2.

$$RCrL(H_2O)^{2+} + Ru(bpy)_3^{3+} \rightarrow RCrL(H_2O)^{3+} + Ru(bpy)_3^{2+} \quad (1)$$

$$RCrL(H_2O)^{2+} + {}^*Cr(bpy)_3^{3+} \rightarrow RCrL(H_2O)^{3+} + Cr(bpy)_3^{2+} \quad (2)$$

The objectives of this study were the evaluation of the rate constants, their correlation with external parameters relating to the oxidation, and the further understanding of the ensuing homolysis reaction, eq 3.

$$RCrL(H_2O)^{3+} \xrightarrow{H_2O} (H_2O)_2CrL^{3+} + R^\bullet \quad (3)$$

Experimental Section

Materials. The Cr(II) complex $(H_2O)_2CrL^{2+}$ was prepared in solution from $CrCl_2 \cdot 4H_2O$[36] and the free ligand (Strem). The organochromium complexes were formed[37] by the reaction of a slight excess of the desired alkyl bromide or iodide with $(H_2O)_2CrL^{2+}$. The products were chromatographed on SP-Sephadex C25, with the desired organochromium fraction being eluted by 0.21 M electrolyte. The complexes were identified by their characteristic UV–visible spectra, which were known from previous work.[37] Several of these complexes were previously unknown, but the same method yielded $RCrL(H_2O)^{2+}$ complexes with R = $CH_2C_6H_4$-4-CF_3, $CH_2C_6H_4$-4-F, $CH_2C_6H_4$-4-Cl, $CH_2C_6H_4$-4-OCH_3, and $CH_2C_6H_4$-4-CN.

$[Cr(bpy)_3](ClO_4)_3$ and its analogues were prepared as before.[38] Solutions of $Ru(bpy)_3^{3+}$ were produced by oxidation of $Ru(bpy)_3^{2+}$ by PbO_2 in 3 M H_2SO_4.[39] The resulting green solution was filtered to remove $PbSO_4$ and unreacted PbO_2.

Products and Stoichiometry. The stoichiometry of the $Ru(bpy)_3^{3+}$ oxidations was determined for $4\text{-}BrC_6H_4CH_2CrL(H_2O)^{2+}$ by spectrophotometric titration at 676 nm, where $Ru(bpy)_3^{3+}$ has $\epsilon = 4.09 \times 10^2$ L mol^{-1} cm^{-1},[40] and at 450 nm, where $Ru(bpy)_3^{2+}$ has $\epsilon = 1.44 \times 10^4$ L mol^{-1} cm^{-1}.

The spectrum of the product of eq 2 (R = 2-butyl) was determined on a point-by-point basis over 510–650 nm at 10-nm intervals. It closely matched the known spectrum of $Cr(bpy)_3^{2+}$. Quantum yields for the formation of $Cr(bpy)_3^{2+}$, defined as $\Phi = [Cr(bpy)_3^{2+}]_\infty/[{}^*Cr(bpy)_3^{3+}]_0$, were determined from the absorbance of the product at 560 nm, where $\epsilon = 4.81 \times 10^3$ L mol^{-1} cm^{-1}.[41] The value of $[{}^*Cr(bpy)_3^{3+}]_0$ was determined in the absence of quencher from the absorbance at 445 nm ($\epsilon = 3 \times 10^3$ L mol^{-1} cm^{-1})[42] shortly after the laser flash.

Kinetics. Laser flash photolysis was the method used to evaluate the rate constants of reactions 1 and 2, with but one exception. The exception was reaction 1 for R = CH_3, where the much lower rate constant required conventional spectrophotometry.

In the case of $^*Cr(bpy)_3^{3+}$, the kinetic measurements were made by following the decay of the emission signal at 727 nm. The solutions had μ = 0.21 M, with $[H^+]$ = 0.010 M, and ionic strength maintained by sodium perchlorate. The organochromium complex was present in excess. The excited state was created with Coumarin 460 (0.15 mM in methanol) used as the laser dye. When the R group was a secondary alkyl, a small amount of Fe^{3+} was added to eliminate any $Cr(bpy)_3^{2+}$ present from prior homolysis of the organochromium complex followed by the reduction of $Cr(bpy)_3^{3+}$ by $R^\bullet$. The observed emission-time profile fit a single exponential with a rate constant given by

$$k_\psi = k^\circ + k[RCrL(H_2O)^{2+}] \quad (4)$$

in which k° represents the rate constant for the inherent decay processes and k the rate constant for reaction 2.

The $Ru(bpy)_3^{3+}$ reactions were also studied by laser flash photolysis. The reaction solution contained $Ru(bpy)_3^{2+}$, a cobalt(III) quencher, and the desired $RCrL(H_2O)^{2+}$ complex. The laser flash at 460 nm produced $^*Ru(bpy)_3^{2+}$, which was in turn quenched oxidatively by a $(NH_3)_5Co^{III}L$ complex (L = Br^-, C_5H_5N, or H_2O).[43–45] The production of $Ru(bpy)_3^{3+}$ is largely complete within the 1-μs time of the laser flash. The subsequent reaction between it and $RCrL(H_2O)^{2+}$ was monitored at 450 nm, the absorption maximum of $Ru(bpy)_3^{2+}$. The kinetic measurements were performed with $[RCrL(H_2O)^{2+}]_0 \geq 10[Ru(bpy)_3^{3+}]_0$.

The data fit first-order kinetics. The rate constants were calculated by a nonlinear least-squares fitting to the equation $D_t = D_\infty + (D_0 - D_\infty)\exp(-k_\psi t)$, where D equals the absorbance or emission intensity.

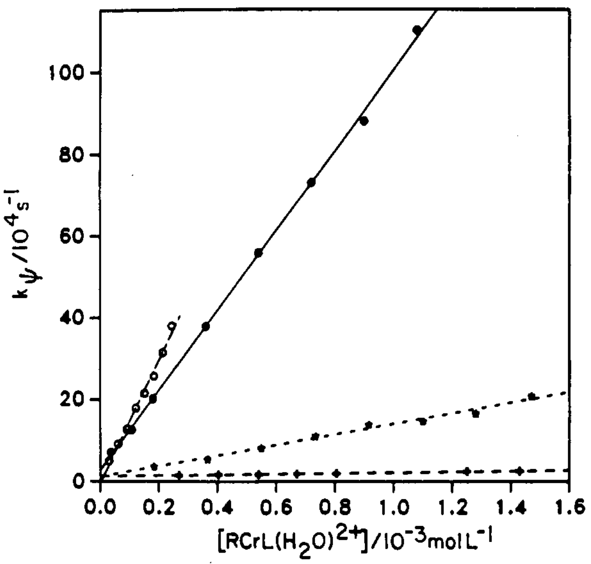

Figure 1. Quenching of $^*Cr(bpy)_3^{3+}$ by $RCrL(H_2O)^{2+}$ plotted according to eq 4. Data are shown for R = 1-C_3H_7 (pluses), 4-$BrC_6H_4CH_2$ (open circles), $C_6H_5CH_2$ (filled circles), and 2-C_4H_9 (stars).

Table I. Rate Constants[a] for the Oxidation of $RCrL(H_2O)^{2+}$ Complexes by $^*Cr(bpy)_3^{3+}$

R	$k/10^7$ L mol^{-1} s^{-1}	R	$k/10^7$ L mol^{-1} s^{-1}
CH_3	0.283 ± 0.050	2-C_4H_9	12.7 ± 0.5
C_2H_5	0.54 ± 0.06	$C_6H_5CH_2$	95 ± 2
1-C_3H_7	0.89 ± 0.04	4-$BrC_6H_4CH_2$	141 ± 4
1-C_4H_9	1.17 ± 0.06	4-$CH_3C_6H_4CH_2$	155 ± 5
2-C_3H_7	10.8 ± 0.7		

[a] At 25.0 °C, 0.010 M H^+, 0.20 M sodium perchlorate (μ = 0.21 M); L = [15]aneN_4.

Table II. Rate Constants[a] for the Oxidation of $C_2H_5CrL(H_2O)^{2+}$ and $(CH_3)_2CHCrL(H_2O)^{2+}$ by ^2E $Cr(NN)_3^{3+}$ Ions

$^*Cr(NN)_3^{3+}$	$k/10^7$ L mol^{-1} s^{-1}		$E^\circ_{3^*/2}$/V
	C_2H_5	$(CH_3)_2CH$	
$Cr(5\text{-}Cl\text{-}phen)_3^{3+}$	1.28 ± 0.10	19.3 ± 1.5	1.53
$Cr(bpy)_3^{3+}$	0.54 ± 0.006	10.8 ± 0.7	1.44
$Cr(5\text{-}Mephen)_3^{3+}$	0.49 ± 0.11	7.4 ± 0.2	1.39
$Cr(4,7\text{-}Me_2bpy)_3^{3+}$	0.38 ± 0.01		1.25
$Cr(4,4'\text{-}Me_2phen)_3^{3+}$		4.5 ± 0.4	1.23

[a] See footnote a of Table I.

Results and Interpretation

$^*Cr(bpy)_3^{3+}$. Quenching of ^2E $Cr(bpy)_3^{3+}$ by the series of $RCrL(H_2O)^{2+}$ complexes was studied with the latter present in substantial excess. All of the reactions followed first-order kinetics, and in every case k_ψ varied linearly with $[RCrL(H_2O)^{2+}]$, as given in eq 4 and illustrated in Figure 1. When R was a secondary alkyl group, Fe^{3+} was added to the solution. The function of Fe^{3+} is to oxidize $Cr(bpy)_3^{2+}$ ($k = 7.3 \times 10^8$ L mol^{-1} s^{-1}),[46] thus eliminating the undesired quenching by $Cr(bpy)_3^{2+}$. Fe^{3+} also

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eliminates any homolysis products present prior to the flash. Without it, a nonlinear plot in eq 4 would have been found.[38,47,48]

The rate constants so obtained are given in Tables I and II. Values were obtained with $^*Cr(bpy)_3^{3+}$ for the entire series of R groups (Table I) and for C_2H_5 and $(CH_3)_2CH$ complexes for several bpy and phen analogues (Table II). The data clearly show the trend methyl < primary alkyl < secondary alkyl < aralkyl. For a given R group, the rate constant increases regularly with the potential of the excited state, as expected for an electron-transfer process. It is also worth noting that an inorganic analogue, $BrCrL(H_2O)^{2+}$, is an ineffective quencher of $^*Cr(bpy)_3^{3+}$ or $^*Cr(5\text{-Cl-phen})_3^{3+}$, $k < 5 \times 10^5$ L mol^{-1} s^{-1}, which establishes that only the organometallic complexes react. From this we infer that energy transfer, which should be effective for both $BrCrL(H_2O)^{2+}$ and $RCrL(H_2O)^{2+}$,[31] is not the process by which the organometallic species react.

The spectrum of the products was taken after the quenching reaction between $^*Cr(bpy)_3^{3+}$ and $2\text{-}C_4H_9CrL(H_2O)^{2+}$. No intermediates were observed, and the only product detected over the range 510–560 nm was $Cr(bpy)_3^{2+}$. Quantum yields for $Cr(bpy)_3^{2+}$ formation were evaluated for primary and secondary alkyl complexes without addition of Fe^{3+}. For $1\text{-}C_3H_7$ and $1\text{-}C_4H_9$, Φ was ca. 0.07, and for $2\text{-}C_3H_7$ and $2\text{-}C_4H_9$, ca. 0.7. This trend is to be expected, because the k° term is considerably more important for the slowly reacting primary alkyls. Also, the homolysis of the oxidized species $RCrL(H_2O)^{3+}$ (eq 3) is expected to be much more rapid when R is a secondary alkyl. The theoretical values of Φ is 2, because a second Cr(II) complex is expected from the reaction

$$R^\bullet + Cr(bpy)_3^{3+} \rightarrow (bpy)_2Cr(bpy\text{-}R)^{2+} + H^+ \qquad (5)$$

The low values of Φ result from the occurrence of back electron transfer, eq 6. That this reaction occurs is evidence that the homolysis of eq 3 is not an exceptionally fast reaction. Other evidence[35] now also supports the observation that homolysis occurs slowly, which is also supported by a stoichiometric factor of 2 in the $Ru(bpy)_3^{3+}$ reaction, as presented subsequently.

$$Cr(bpy)_3^{2+} + RCrL(H_2O)^{3+} \rightarrow Cr(bpy)_3^{3+} + RCrL(H_2O)^{2+} \qquad (6)$$

$Ru(bpy)_3^{3+}$. Two titrations were performed to determine the reaction stoichiometry. In the first, $4\text{-}BrC_6H_4CH_2CrL(H_2O)^{2+}$ was titrated with $Ru(bpy)_3^{3+}$, and in the second, the order was reversed. These trend toward two limiting situations, depending on whether or not $Ru(bpy)_3^{3+}$ was present in excess during the titration. In the first of these, the endpoint occurred at an approximate 1:1 ratio, consistent with eq 1. The reverse titration displayed the endpoint at a ratio $Ru(bpy)_3^{3+}$: $RCrL(H_2O)^{2+}$ = 2:1. The reason is that in the second case the $R^\bullet$ from slow homolysis, eq 3, is able to undergo a subsequent reaction with excess Ru(III):

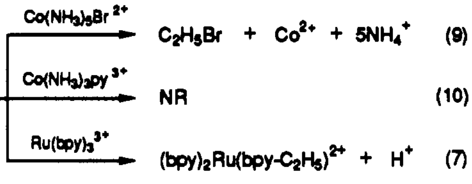
$$R^\bullet + Ru(bpy)_3^{3+} \rightarrow (bpy)_2Ru(bpy\text{-}R)^{2+} + H^+ \qquad (7)$$

The kinetic data, obtained with $[RCrL(H_2O)^{2+}]_0 \gg [Ru(bpy)_3^{3+}]_0$, fit excellently to first-order kinetics. The values of k_ψ are directly proportional to $[RCrL(H_2O)^{2+}]$, confirming the second-order rate law, eq 8. The values of k determined from

$$d[Ru(bpy)_3^{2+}]/dt = k[Ru(bpy)_3^{3+}][RCrL(H_2O)^{2+}] \qquad (8)$$

experiments in which $Co(NH_3)_5Br^{2+}$ was the quencher are summarized in Table III. As with the $^*Cr(bpy)_3^{3+}$ reaction, the rate constants again increase in the order methyl < primary alkyl < secondary alkyl < aralkyl.

For the complex $C_2H_5CrL(H_2O)^{2+}$, experiments were also done with $Co(NH_3)_5py^{3+}$ and $Co(NH_3)_5OH_2^{3+}$ as quenchers for $^*Ru(bpy)_3^{2+}$. The values of k are 2.06×10^4 (py) and 2.04×10^4 L mol^{-1} s^{-1} (OH_2), as compared to 2.13×10^4 L mol^{-1} s^{-1} (Br). The fact that all three quenchers give the same rate constant needs to be explained. On the one hand, the rate constant might not be expected to depend on the identity of the cobalt reagent, since it merely serves as the quencher by which $Ru(bpy)_3^{3+}$ is prepared. On the other hand, a factor of 2 was found for $(H_2O)_5CrC_2H_5^{2+}$ between the quenchers $Co(NH_3)_5py^{3+}$ and $Co(NH_3)_5Br^{2+}$ ($k^{py}/k^{Br} = 2.15 \pm 0.14$).[33] The reason given is the competition between the following three reactions of $^\bullet C_2H_5$:



With $Co(NH_3)_3Br^{2+}$ as quencher ($k_9 = 2.6 \times 10^6$ L mol^{-1} s^{-1}),[49] the rate is simply k_1 (equivalent of eq 1). With $Co(NH_3)_5py^{3+}$ as quencher ($k_{10} < 10^5$),[49] however, reaction 7 occurs; as a result a second $Ru(bpy)_3^{3+}$ is reduced. The experimental value of k for $(H_2O)_5CrC_2H_5^{2+}$ is therefore $2k_1$.

With the macrocycle, the rate of bond homolysis of $C_2H_5CrL(H_2O)^{3+}$ (eq 3) is evidently slow enough that reaction 1 is complete before reaction 7 can occur. The radical either dimerizes/disproportionates or reacts with a Co(III) quencher. Regardless of quencher, therefore, each experiment measures only k_1. The complex $1\text{-}C_3H_7CrL(H_2O)^{2+}$ gave an intermediate rate

Table III. Rate Constants[a] for the Oxidation of $RCrL(H_2O)^{2+}$ by $Ru(bpy)_3^{3+}$

R	k/L mol^{-1} s^{-1}
CH_3	14.2 ± 0.5
C_2H_5	$(2.13 \pm 0.04) \times 10^4$
$1\text{-}C_3H_7$	$(3.50 \pm 0.09) \times 10^3$
$1\text{-}C_4H_9$	$(3.80 \pm 0.09) \times 10^3$
$2\text{-}C_3H_7$	$(4.74 \pm 0.25) \times 10^6$
$2\text{-}C_4H_9$	$(1.42 \pm 0.08) \times 10^6$
$c\text{-}C_6H_{11}$	$(1.18 \pm 0.03) \times 10^7$
$4\text{-}CF_3C_6H_4CH_2$	$(2.72 \pm 0.11) \times 10^7$
$4\text{-}FC_6H_4CH_2$	$(2.95 \pm 0.03) \times 10^8$
$4\text{-}ClC_6H_4CH_2$	$(3.84 \pm 0.21) \times 10^8$
$4\text{-}BrC_6H_4CH_2$	$(4.27 \pm 0.08) \times 10^8$
$C_6H_5CH_2$	$(5.51 \pm 0.21) \times 10^8$
$4\text{-}CH_3C_6H_4CH_2$	$(1.05 \pm 0.02) \times 10^9$
$4\text{-}CH_3OC_6H_4CH_2$	$(1.23 \pm 0.04) \times 10^9$

[a] See footnote a of Table I.

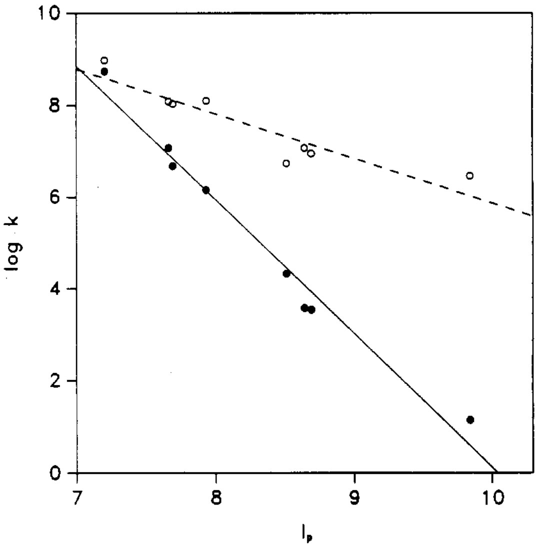


Figure 2. Linear free energy correlation for the rates of oxidation of $RCrL(H_2O)^{2+}$ by $Ru(bpy)_3^{3+}$ (filled circles) and $^*Cr(bpy)_3^{3+}$ (open circles). The plot depicts the variation of log k with the ionization potential of the free radical $R^\bullet$.

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(48) Fe^{3+}, added at concentrations 2.7–10.7 mM, had no effect on k. A concentration of 2.7 mM was used in most of these experiments.

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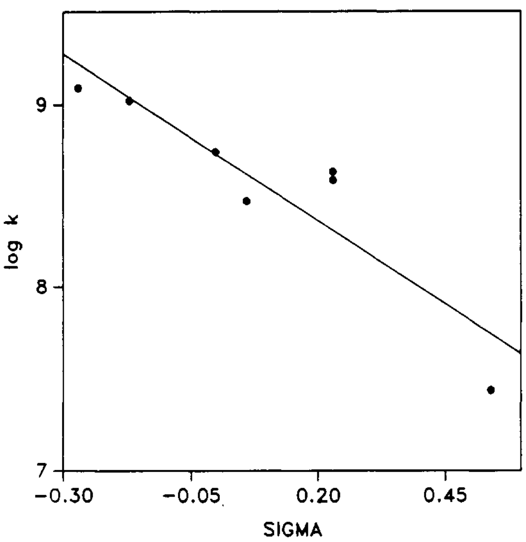

Figure 3. Plot of log k for the oxidation of $4\text{-}XC_6H_4CH_2CrL(H_2O)^{2+}$ by $Ru(bpy)_3^{3+}$ versus the Hammett σ parameter for substituent X.

ratio ($k^{py}/k^{Br} = 1.4$), suggesting that for it the rates of reactions 3 and 7 are comparable.

Discussion

The reactivity of the $RCrL(H_2O)^{2+}$ complexes toward $Ru(bpy)_3^{3+}$ is very sensitive to the identity of the group R. In all, the rates vary by a factor of $\sim 10^8$ along the series. A similar trend is seen in the $^*Cr(bpy)_3^{3+}$ rate constants, although here the reactivity is so much higher that the selectivity is less. The rates vary by a factor of only about 10^3 along the same series of R's.

We have thus made an effort to relate the measured rate constants to a fundamental parameter concerned with the electron-donating ability of the $RCrL(H_2O)^{2+}$ complexes. The ideal parameter would be values of $E°$ for the $RCrL(H_2O)^{3+/2+}$ couples. These, unfortunately, are currently unavailable. Thus we turned to the gas-phase ionization potentials of the alkyl radicals themselves, which have been measured by photoelectron spectroscopy.[50-53] For both series of reactions, Figure 2 depicts a plot of log k versus the ionization potential. Both series give a reasonable linear free energy correlation. This affirms that the nature of the reaction is indeed electron transfer.

In the series of $Ru(bpy)_3^{3+}$ reactions, rate constants were determined for a number of para-substituted benzyl groups (Table III). The more electron-donating substituents (e.g. CH_3O and CH_3) react more rapidly, whereas the smallest rate constant is that for CF_3, the substituent with the most positive σ value. A correlation according to the Hammett equation $\log k_x = \log k_H + \sigma\rho$ is shown in Figure 3. The reaction constant, given as the slope of this line, is $\rho = -2.0$.

The final question we would address concerns the rate at which the oxidized organochromium macrocycle undergoes homolysis in eq 3. A kinetic simulation was conducted for the overall scheme for $R = C_2H_5$. The value of k_3 was varied until the same rate was obtained for eq 1, regardless of whether $Co(NH_3)_5Br^{2+}$ or $Co(NH_3)_5py^{3+}$ was used as quencher. A value $k_3 < \sim 20\ s^{-1}$ was sufficient to account for the finding. If this same value of k_3 is assumed to apply to $1\text{-}C_3H_7CrL(H_2O)^{3+}$, it is possible through the same simulation to calculate the expected values of k with the two quenchers. (The value of k for the 1-propyl complex is smaller than for ethyl, and so the ratio between k^{py} and k^{Br} is not necessarily unity.) The simulation yields $k^{py}/k^{Br} = 1.5$, in reasonsable agreement with the experimental ratio of 1.4.

Conclusions. The family of $RCrL(H_2O)^{2+}$ complexes reacts with $Ru(bpy)_3^{3+}$ and $^*Cr(bpy)_3^{3+}$ by electron transfer. The rate constants for electron transfer respond to a given alkyl or aralkyl group R such that k increases with the electron-donating ability of R, as measured by its ionization potential or Hammett σ constant. The resultant oxidized organometals $RCrL(H_2O)^{3+}$ undergo homolysis much more slowly than the pentaaqua analogues $(H_2O)_5CrR^{3+}$.

Acknowledgment. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-Eng-82.

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Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Further Studies on the Role of Neighboring Group Participation in CO Substitution Reactions of Group 6 Metal Carboxylates

Donald J. Darensbourg,* Jennifer A. Joyce, Christopher J. Bischoff, and Joseph H. Reibenspies

Received July 18, 1990

The reactions between $W(CO)_5O_2CR^-$ ($R = -C(CH_3)_3$, $-CH_2CN$, and $-CF_3$) and $P(OCH_3)_3$ result in cis CO replacement via a dissociative mechanism with concomitant formation of *cis*-$W(CO)_4[P(OCH_3)_3]O_2CR^-$. From the temperature dependence of the rate constants, activation parameters for the reactions where $R = -CH_2CN$ and $-C(CH_3)_3$ were determined to be $\Delta H^* = 25.3 \pm 0.8$ kcal·mol^{-1} and $\Delta S^* = 7.7 \pm 2.5$ eu and $\Delta H^* = 24.2 \pm 1.5$ kcal·mol^{-1} and $\Delta S^* = 9.7 \pm 5.1$ eu, respectively. These rate data, coupled with those previously reported for $R = -CH_3$ and $-H$, display a linear free energy relationship when plotted against Taft's polar substituent constant, σ^*. The reaction constant, ρ^*, was found to be -0.66, indicating the CO substitution reaction to be facilitated by electron-releasing substituents. This observation, taken together with the ability of the carboxylate ligand to chelate to the metal center, is interpreted as involvement of the distal oxygen atom of the monodentate carboxylate in cis CO substitution reactions. The X-ray structure of the cyanoacetate derivative, $[Et_4N][W(CO)_5O_2CCH_2CN]$, is also reported. The complex crystallizes in the triclinic centrosymmetric space group $P\bar{1}$ (No. 2) with $a = 7.292$ (2) Å, $b = 11.552$ (4) Å, $c = 12.564$ (4) Å, $\alpha = 76.03$ (3)°, $\beta = 73.65$ (2) Å, $\gamma = 86.48$ (2) Å, $V = 985.6$ (5) Å^3, and $Z = 2$. Refinement converged at $R = 2.36\%$ and $R_w = 3.23\%$ for those 3380 reflections with $I > 2\sigma(I)$ and $T = 193$ K.

Introduction

As part of our continuing interest in the insertion chemistry of carbon dioxide into group 6 M–H and M–CH_3 bonds, we have investigated the kinetic parameters for CO dissociation in the resultant $M(CO)_5O_2CR^-$ ($R = H, CH_3$) derivatives.[1,2] Of particular concern is the role of metal unsaturation as a conse-

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