stable than binuclear products of the corresponding reactions of the iron nitrosyl analogues **3** and **5**, which could not even be detected before undergoing fragmentation. Furthermore, the course of the alkylation reactions of $[(CO)_3\overline{Fe(\mu\text{-PPh}_2)(\mu\text{-}}$ $\overline{CO)Fe(CO)_2(PPh_2R)}]^-$ contrasts sharply with that of the alkylation reactions of **3** and **5**, as already mentioned earlier for $[(CO)_3Fe(\mu\text{-PR}_2)_2Fe(CO)_3]^{2-}$ vis-à-vis **2**. The foregoing differences in behavior underscore a much greater propensity of metal–alkyl complexes to undergo migratory insertion of CO compared to that of NO.[24] Also, of the two binuclear iron systems studied in this laboratory, the nitrosyl complexes generally react more readily by the coupling of $\mu\text{-PR}_2$ with H or R.

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Electron-Transfer Reactions between Pentaaquo(organo)chromium(2+) and Tris(bipyridyl)ruthenium(3+) Ions[1]
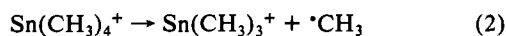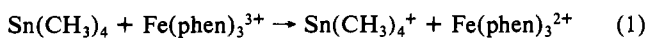
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The ruthenium complex Ru(bpy)$_3^{3+}$, generated by laser flash photolysis, reacts with a wide range of (H$_2$O)$_5$CrR^{2+} complexes. The first step in the sequence is attributed to the one-electron oxidation of the organochromium cation. This step is accompanied by formation of Ru(bpy)$_3^{2+}$. The rate constants (i-Pr > Et >> Me) correlate with the ionization potentials of the free radicals R$^\bullet$. Values for para-substituted benzylchromium ions follow the Hammett correlation. The immediate product of electron transfer, CrR^{3+}, can undergo homolysis, as found for R = Et by kinetic tests and radical trapping, or in suitably constituted cases it can react by internal electron transfer, e.g., CrCH$_2$OCH$_3^{3+}$ + H$_2$O → Cr^{2+} + CH$_3$OCH$_2$OH + H$^+$.

Introduction

One important question for metal–alkyl complexes is the relation between the lability of a metal–carbon bond and the oxidation state of the metal.[2–4] A better understanding of this relation may assist in synthesis and in homogeneous catalysis, where alkylmetal complexes are often intermediates.[5] One way to labilize metal–carbon bonds is via oxidative homolysis: a one-electron oxidation yields an oxidized species that undergoes homolytic dissociation. This has been well studied for main-group-metal alkyls, e.g., the reaction of SnR$_4$ with the strong one-electron oxidants such as IrCl$_6^{2-}$ and iron(III) phenanthroline complexes:[6]

$$Sn(CH_3)_4 + Fe(phen)_3^{3+} \rightarrow Sn(CH_3)_4^+ + Fe(phen)_3^{2+} \quad (1)$$

$$Sn(CH_3)_4^+ \rightarrow Sn(CH_3)_3^+ + {}^\bullet CH_3 \quad (2)$$

One characteristic of these reactions is the rate increase in the series Me < Et < *sec*-Bu. This is consistent with rate-limiting electron transfer, rather than with electrophilic substitution, as found for dealkylations by Ag(I), Cu(I), and Cu(II).[2]

Analogous reactions are less well-known for transition-metal alkyls. Among the reactions that have been characterized are the oxidations of R$_2$Co(chel)[7] and RCo(chel)[4,8–10] complexes (where chel = a chelating or macrocyclic ligand system) by IrCl$_6^{2-}$ or iron(III) phenanthroline complexes. These reactions (eq 3) yield

$$RCo^{III}(chel) + IrCl_6^{2-} \rightarrow RCo^{IV}(chel)^+ + IrCl_6^{3-} \quad (3)$$

an oxidized organocobalt complex that can undergo either nucleophilic solvolysis (eq 4a) or homolysis (eq 4b).

When the alkyl cobaloxime complexes RCo(dmgH)$_2$ are oxidized by IrCl$_6^{2-}$, the reaction[8] follows the pathway described by

(1) Based in part on the Ph.D. thesis of J.D.M., Iowa State University, 1986.
(2) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic: New York, 1978.
(3) Halpern, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 274.
(4) Vol'pin, M. E.; Levitin, I. Ya.; Sigan, A. L.; Nikitaev, A. T. *J. Organomet. Chem.* **1985**, *279*, 263.
(5) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980.
(6) Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5593.

(7) Tamblyn, W. H.; Klingler, R. J.; Hwang, W. S.; Kochi, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 3161. Oxidative homolysis has also been reported for a series of R$_2$Fe(bpy)$_2^+$ complexes (Lau, W.; Huffman, J. C.; Kochi, J. K. *Organometallics* **1982**, *1*, 155) and dialkylplatinum(II) complexes (Chen, J. Y.; Kochi, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 1450).
(8) Halpern, J.; Chan, M. S.; Roche, T. S.; Tom, G. M. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 141.
(9) Vol'pin, M. E.; Levitin, I. Ya.; Sigan, A. L. *Inorg. Chim. Acta* **1980**, *41*, 271.
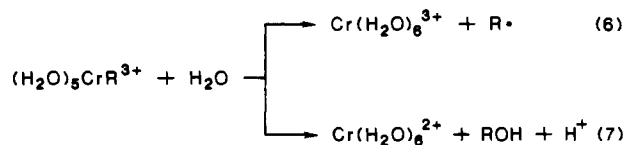(10) Fanchiang, Y.-T. *Organometallics* **1983**, *2*, 121.

$$RCo^{IV}(chel)^+ \begin{cases} \xrightarrow{+H_2O} ROH + Co^{II}(chel) + H^+ & (4a) \\ \xrightarrow{+H_2O} R\cdot + Co^{III}(chel) & (4b) \end{cases}$$
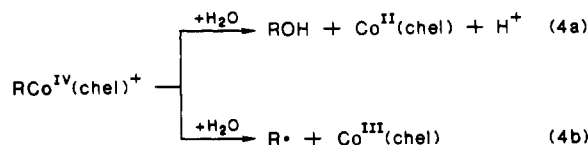
eq 3–4a, whereas homolytic cleavage of the cobalt–carbon bond occurs for the chelate systems acacen and sal₂en, bis(acetylacetone) ethylenediimine and bis(salicylaldehyde) ethylenediimine, respectively.[9]

Some results pertinent to the general question have been obtained in the series of complexes of interest in this work, organochromium cations with the general formula $(H_2O)_5CrR^{2+}$. In many instances, these complexes do not react directly with oxidants; rather, Cr^{2+} and $R\cdot$, the fragments of the spontaneous, unimolecular homolytic bond cleavage, are subsequently oxidized.[11,12] In a few cases, however, direct oxidation has been reported. Among these cases are the complexes in which R is an α-OH or α-OR group, in which case Cu^{2+}, Fe^{3+}, Hg^{2+}, and VO^{2+} react directly.[13] In addition, we have recently found that the nitrosonium ion, NO^+, derived from nitrous acid, functions as a rather general oxidizing reagent for this family of organochromium complexes.[1,14]

These results made it clear that only relatively powerful electron acceptors will be able to react directly with the CrR^{2+} complexes. In addition, a suitable oxidant will most likely have structural and electronic properties that promote an outer-sphere mechanism for electron transfer. Tris(2,2′-bipyridyl)ruthenium(3+) ion satisfies these requirements. The ion $Ru(bpy)_3^{3+}$ is a powerful oxidant, with $E° = +1.26$ V for the couple $Ru(bpy)_3^{3+}/Ru(bpy)_3^{2+}$.[15] The electronic configurations (d^5 and d^6, respectively) and the lack of dissociation of the bipyridyl chelating ligand from either oxidation state provide the factors that favor an electron-transfer process. Since the complex $Ru(bpy)_3^{3+}$ can be prepared by flash photolytic techniques that are compatible with the chemical and other characteristics of the CrR^{2+} complexes, we undertook an investigation of the reaction shown in eq 5 for a series of such

$$(H_2O)_5CrR^{2+} + Ru(bpy)_3^{3+} \rightarrow (H_2O)_5CrR^{3+} + Ru(bpy)_3^{2+} \quad (5)$$
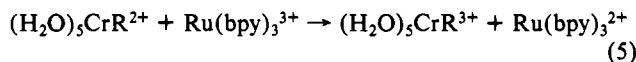
complexes. The results of these determinations establish that direct electron transfer indeed occurs with the rate constants spanning over 5 orders of magnitude. From these data can be drawn inferences concerning the mechanism of electron transfer and the subsequent fate of the oxidized CrR^{3+} complex, whether it decomposes by homolysis (eq 6) or hydrolysis (eq 7) or some other process.

$$(H_2O)_5CrR^{3+} + H_2O \begin{cases} \longrightarrow Cr(H_2O)_6^{3+} + R\cdot & (6) \\ \longrightarrow Cr(H_2O)_6^{2+} + ROH + H^+ & (7) \end{cases}$$

Results and Interpretations

General Observations. The reactions of the CrR^{2+} complexes with $Ru(bpy)_3^{3+}$ were studied by the use of laser flash photolysis. The charge-transfer excited state, $[Ru(bpy)_3^{2+}]^*$, was produced by irradiation of the metal-to-ligand charge-transfer band of $Ru(bpy)_3^{2+}$ centered at 450 nm in the presence of a suitable oxidative quencher, often $Co(NH_3)_5Br^{2+}$.[15-19] This produces the

(11) Espenson, J. H. *Adv. Inorg. Bioinorg. React. Mech.* **1982**, *1*, 1.
(12) Espenson, J. H. *Prog. Inorg. Chem.* **1983**, *30*, 189.
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(14) Melton, J. D.; Bakac, A.; Espenson, J. H., submitted for publication.
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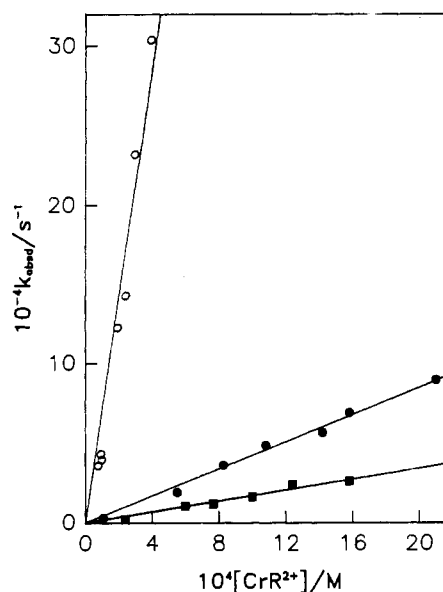
Figure 1. Linear plots of k_{obsd} vs. $[CrR^{2+}]$ for the reactions of several organochromium complexes. Data are shown for $CrCH(CH_3)_2^{2+}$ (filled circles), $CrCH_2Ph^{2+}$ (open circles), and $CrCH_2C_6H_4$-p-CF_3^{2+} (squares).

Table I. Rate Constants for the Reactions of Tris(2,2′-bipyridyl)ruthenium(III) with $(H_2O)_5CrR^{2+}$ [a]

R	$k/M^{-1} s^{-1}$	R	$k/M^{-1} s^{-1}$
p-$CH_2C_6H_4CH_3$	2.9×10^8	CH_2OCH_3	1.04×10^7
$CH_2C_6H_5$	5.3×10^8	$CH(CH_3)_2$	4.25×10^7
p-$CH_2C_6H_4CF_3$	1.71×10^7	CH_2CH_3	2.00×10^5
p-$CH_2C_6H_4CN$	9.5×10^6	CH_3	$<10^3$

[a] $T = 25.0$ °C; $I = 0.10$ M.

ruthenium(III) complex $Ru(bpy)_3^{3+}$. Thus a fluorescence cell containing an acidic solution of $Ru(bpy)_3^{2+}$, $(NH_3)_5CoBr^{2+}$, and CrR^{2+} was irradiated by a 0.6-μs laser pulse centered at 461 (± 20) nm.

The absorbance of the solution was monitored at 450 nm, recording primarily the change in $[Ru(bpy)_3^{2+}]$. Immediately upon the laser pulse, the absorbance dropped; during that time (1–2 μs) the photochemical excitation and quenching reactions were completed. Following that, the absorbance rose with time as the reaction between $Ru(bpy)_3^{3+}$ and CrR^{2+} (eq 5) occurred. The absorbance returned to its initial value, or sometimes just slightly less.

Kinetics. The concentrations used in these experiments were typically as follows: $[Ru(bpy)_3^{2+}]_0 = (1.2-2.6) \times 10^{-5}$ M, $[(NH_3)_5CoBr^{2+}]_0 = (2-10) \times 10^{-3}$ M, and $[(H_2O)_5CrR^{2+}]_0 = (2-210) \times 10^{-5}$ M. The laser pulse and quenching reaction typically produced an initial concentration of $\sim 1 \times 10^{-5}$ M $Ru(bpy)_3^{3+}$ in a solution having $[H^+] = 0.07-0.095$ M at $\mu = 0.10$ M and $T = 25$ °C. Since $[CrR^{2+}]_0 >> [Ru(bpy)_3^{3+}]_0$, the reactions followed pseudo-first-order kinetics for 3 or more half-lives. Values of k_{obsd} from the individual experiments are tabulated in the thesis cited.[1]

Plots of k_{obsd} vs. $[CrR^{2+}]$ were linear. Typical plots are shown in Figure 1. This behavior is consistent with a second-order rate law, eq 8. The values of k_5, the second-order rate constants, are given in Table I.

$$-d[Ru(bpy)_3^{3+}]/dt = k_5[Ru(bpy)_3^{3+}][CrR^{2+}] \quad (8)$$

Use of a Different Co(III) Quencher: Test for a Radical Intermediate. As cited in the Introduction, it is reasonable (but not certain) that the reaction between $Ru(bpy)_3^{3+}$ and CrR^{2+} results

(17) Sutin, N.; Creutz, C. *Pure Appl. Chem.* **1980**, *52*, 2717.
(18) Sutin, N.; Creutz, C. *J. Chem. Educ.* **1983**, *60*, 809.
(19) (a) Lytle, F. E.; Hercules, D. M. *J. Am. Chem. Soc.* **1969**, *91*, 253. (b) Kimura, M.; Nishida, S. *J. Chem. Soc., Dalton Trans.* **1985**, 355.
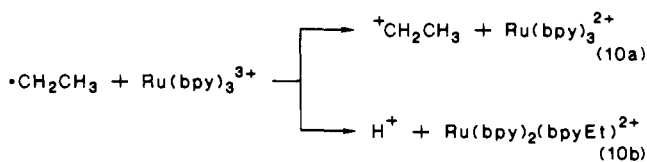
in oxidative homolysis and that a free alkyl radical would be formed (eq 6). Alternatively, solvolysis of CrR^{3+} would lead to the reducing species Cr^{2+} (eq 7). Therefore, experiments were sought to address these possibilities.

Consider first the situation that would prevail were the alkyl radical formed in the experiments described. It would be expected to reduce the cobalt(III) quencher, as in eq 9. Such reactions

$$R^{\bullet} + (NH_3)_5CoBr^{2+} \xrightarrow{H^+} RBr + Co_{aq}^{2+} + 5NH_4^+ \quad (9)$$

have been reported for cyclopentyl and 1-methylethyl (i.e., 2-propyl) radicals,[20] and it is reasonable to suggest an analogous reaction for the ethyl radical, the case that was tested here. This type of reaction finds precedent in the reactions of $CH_3CH_2^{\bullet}$ with $IrCl_6^{2-}$ [21] and with $CuCl_2$,[22] which produce ethyl chloride. Although the rates of the reactions with $(NH_3)_5CoBr^{2+}$ have not been measured, they must occur fairly rapidly (e.g., $k_9 > 10^6$ M^{-1} s^{-1}) since they occur to the exclusion of bimolecular radical recombination and dimerization processes.

We sought to check this point by replacing the indicated quencher with a similar species that would not be expected to react with an alkyl radical. The pyridine comlex $(NH_3)_5Co(py)^{3+}$ appeared to be a good choice, since it is known to quench the excited state[16d] but has no ligand that can function as an electron-transfer bridge. The latter is a requirement for the reaction in eq 9 to occur efficiently, given that the alkyl halide product signals an inner-sphere mechanism. The alkyl radical, if it cannot react with the Co(III) complex, would necessarily undergo an alternative reaction. There is now good evidence[23] that alkyl radicals, ethyl included, react with $Fe(phen)_3^{3+}$ and $Ru(phen)_3^{3+}$, either to be oxidized directly or to substitute at the 4-position of one phenanthroline ring. Assuming that the same reactions occur for $Ru(bpy)_3^{3+}$, the competing processes are as represented in eq 10a and 10b, respectively. If the relative rates of eq 10a and 10b in water are the same as in acetonitrile,[23] then the latter should predominate by roughly a 4:1 ratio.[24]

$$\bullet CH_2CH_3 + Ru(bpy)_3^{3+} \begin{cases} \longrightarrow {}^+CH_2CH_3 + Ru(bpy)_3^{2+} & (10a) \\ \\ \longrightarrow H^+ + Ru(bpy)_2(bpyEt)^{2+} & (10b) \end{cases}$$

Regardless of which prevails, the occurrence of eq 10 rather than eq 9 will result in measurable changes. The consumption of the additional Ru(III) in eq 10, provided it occurs more rapidly than eq 5, would alter the stoichiometric consumption of reactants, changing $\Delta(Ru(bpy)_3^{3+})$: $\Delta(CrR^{2+})$ from 1:1 with $(NH_3)_5CoBr^{2+}$ quencher to 2:1 with $(NH_3)_5Copy^{3+}$. This change will immediately be reflected in the rate law, with eq 8 being replaced by

$$-d[Ru(bpy)_3^{3+}]/dt = 2k_5[Ru(bpy)_3^{3+}][CrR^{2+}] \quad (11)$$

This prediction has been confirmed experimentally. Figure 2 shows plots of k_{obsd} vs. $[CrCH_2CH_3^{2+}]$ from two series of experiments. The upper line, obtained by using $(NH_3)_5Co(py)^{3+}$ as the quencher, has a slope of $(4.3 \pm 0.2) \times 10^5$ M^{-1} s^{-1}. The lower line, obtained for $(NH_3)_5CoBr^{2+}$, has a slope of $(2.00 \pm 0.05) \times 10^5$ M^{-1} s^{-1}. The ratio of the slopes is 2.15 ± 0.15, which agrees with the prediction within the experimental error, confirming the formulation given. This is consistent with an ethyl radical being formed, which then undergoes the alternative reactions of eq 9 or 10, depending on the cobalt(III) complex employed.

Actually, these series of experiments really verify the likely formation of an intermediate (but not necessarily the ethyl radical)
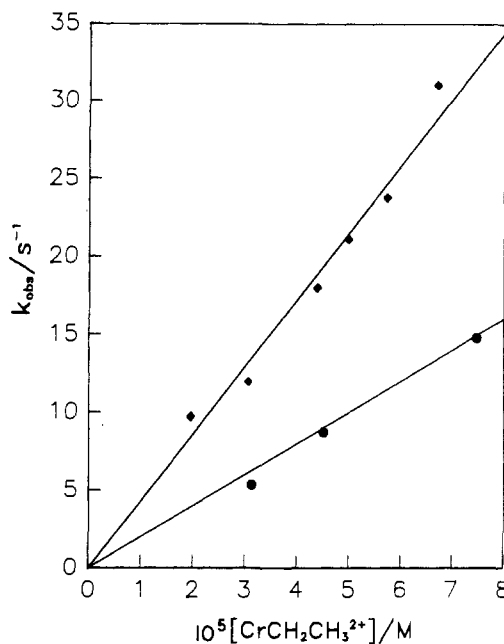
Figure 2. Plots of the pseudo-first-order rate constant for the reaction of $CrCH_2CH_3^{2+}$ with $Ru(bpy)_3^{3+}$ against $[CrCH_2CH_3^{2+}]$ for the series of experiments using the quenchers $(NH_3)_5CoBr^{2+}$ (circles) and $(NH_3)_5Co(py)^{3+}$ (diamonds). The slopes differ by a factor of 2.1_5, as compared to the theoretical factor of 2.00 (see text).

that is capable of distinguishing between the two cobalt complexes in terms of large rate differences and capable of reducing $Ru(bpy)_3^{3+}$. Any intermediate fitting these requirements can account for the results obtained. There is a very real alternative in this system, namely Cr_{aq}^{2+}. Not only might it be formed (see, for example, eq 7), but it also fits the other requirements. In particular, Cr^{2+} reacts much more rapidly with $(NH_3)_5CoBr^{2+}$ ($k = 1.4 \times 10^6$ M^{-1} s^{-1} [25]) than with $(NH_3)_5Co(py)^{3+}$ ($k = 3.8 \times 10^{-4}$ M^{-1} s^{-1} [26]). Also, Cr^{2+} reacts rapidly with $Ru(bpy)_3^{3+}$ (eq 12). We determined the rate constants for this reaction as $k_{12} = (7.6 \pm 0.3) \times 10^7$ M^{-1} s^{-1}.

$$Ru(bpy)_3^{3+} + Cr(H_2O)_6^{2+} \rightarrow Ru(bpy)_3^{2+} + Cr(H_2O)_6^{3+} \quad (12)$$
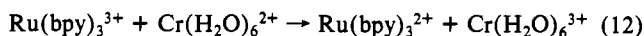
Reaction Product. The determination of the organic product(s) of the reaction will provide a more direct test for the fate of the ethyl group, although it is not a definitive test for the mechanism by which the product is formed. Analysis by GC of the reaction products obtained by steady-state photolysis (see Experimental Section) showed that ethyl bromide was formed in quantitative yield when the quencher was $(NH_3)_5CoBr^{2+}$. This is consistent with the formation of ethyl radicals (eq 6) and with their reaction with this cobalt(III) complex (eq 9).

Reaction of $CrCH_2OCH_3^{2+}$. In contrast to the distinctly different rate constants obtained for the ethyl complex (see Figure 2 and text), similar values with both quenchers were obtained for $CrCH_2OCH_3^{2+}$ as shown in Figure 3. The second-order rate constants, evaluated separately, are $k_5 = (1.04 \pm 0.02) \times 10^7$ and $(1.18 \pm 0.07) \times 10^7$ M^{-1} s^{-1} with $(NH_3)_5CoBr^{2+}$ and $(NH_3)_5Co(py)^{3+}$, respectively, as quenchers. These appear to be equivalent within the error; if all the values are treated as lying on a single line, the average value of k_5 is $(1.06 \pm 0.08) \times 10^7$ M^{-1} s^{-1}. The radical $\bullet CH_2OCH_3$, were it formed, would surely reduce $(NH_3)_5CoBr^{2+}$ rapidly.[27,28a] It might even be a sufficiently strong and facile reductant to react with $(NH_3)_5Co(py)^{3+}$,[28] although the latter would probably not be able to compete with

(20) Espenson, J. H.; Connolly, P.; Meyerstein, D.; Cohen, H. *Inorg. Chem.* **1983**, *22*, 1009.
(21) Steenken, S.; Neta, P. *J. Am. Chem. Soc.* **1982**, *104*, 1244.
(22) Kochi, J. K. *J. Am. Chem. Soc.* **1956**, *78*, 4815.
(23) Rollick, K. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 1319.
(24) The 4:1 ratio is the value expected from the reaction between *n*-Pr* and Ru(phen)₃³⁺.[23] The reactivity of Et* is likely to favor eq 10b even more.

(25) Candlin, J. P.; Halpern, J. *Inorg. Chem.* **1965**, *4*, 766.
(26) Nordmeyer, F.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1162.
(27) Cohen, H.; Meyerstein, D. *J. Chem. Soc., Dalton Trans.* **1977**, 1056.
(28) (a) Espenson, J. H.; Shimura, M.; Bakac, A. *Inorg. Chem.* **1982**, *21*, 2537. (b) Bakac, A.; Butkovic, V.; Espenson, J. H.; Marcec, R.; Orhanovic, M. *Inorg. Chem.* **1986**, *25*, 341.
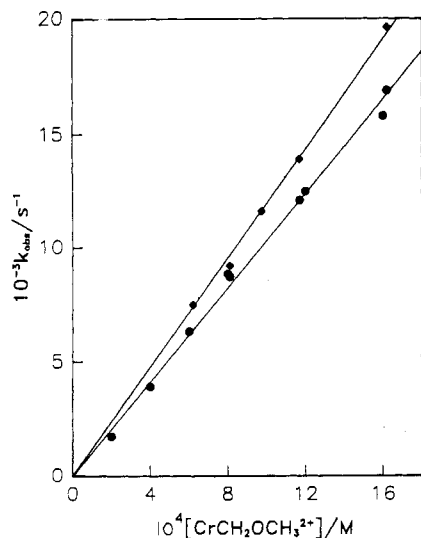
Figure 3. Plots of k_{obsd} vs. $[CrCH_2OCH_3^{2+}]$ for the reaction with Ru-$(bpy)_3^{3+}$ when $(NH_3)_5CoBr^{2+}$ (circles) and $(NH_3)_5Co(py)^{3+}$ (diamonds) are used as quenchers. The slopes of the lines differ only slightly, as expected. (See text and ref 29.)

Ru(bpy)$_3^{3+}$ for the radical. The rate constants obtained with the two quenchers should thus differ by a factor of 2, as observed in the case of $(H_2O)_5CrCH_2CH_3^{2+}$. Since this was not observed, it is unlikely that the radical is formed.

Given the chemical characteristics, the oxidized organo-chromium complex, $CrCH_2OCH_3^{3+}$, would not be expected to undergo homolysis. Rather, it is more likely that this complex will yield Cr^{2+} and $HOCH_2OCH_3$ (the latter will decompose to HCHO and CH_3OH), as in eq 13.

$$(H_2O)_5CrCH_2OCH_3^{3+} + 2H_2O \rightarrow$$
$$Cr(H_2O)_6^{2+} + CH_3OCH_2OH + H^+ \quad (13)$$
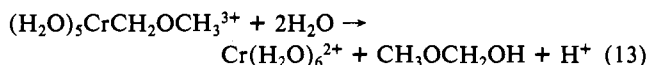
Indeed, this reaction has been identified as occurring when this organochromium cation is oxidized by NO^+. The fate of the Cr^{2+} produced in eq 13 is preferentially to react with $(NH_3)_5CoBr^{2+}$ ($k = 1.4 \times 10^6$ M^{-1} s^{-1}) rather than with $Ru(bpy)_3^{3+}$ ($k = 7.6 \times 10^7$ M^{-1} s^{-1}), given their respective concentrations. When, on the other hand, the quencher is $(NH_3)_5Co(py)^{3+}$, then the Cr^{2+} is more likely to accumulate unreacted during the time of the $Ru(bpy)_3^{3+}$ reduction, rather than to react with this slowly reacting cobalt(III) quencher or with $Ru(bpy)_3^{3+}$ (the pertinent rate constants and concentrations show that $Ru(bpy)_3^{3+}$ will react preferentially with $CrCH_2OCH_3^{2+}$). As a result of the failure of Cr^{2+} and $Ru(bpy)_3^{3+}$ to react to an appreciable extent under these conditions, the rate law of eq 8 rather than eq 11 applies, and nearly the same[29,30] rate constants are expected, as observed, for both quenchers, as depicted in Figure 3.

Discussion

The Electron-Transfer Step. The rate law establishes that the reaction is first order with respect to both $[CrR^{2+}]$ and $[Ru(bpy)_3^{3+}]$. The absorbance rise accompanying this stage of the reaction corresponds to the quantitative re-forming of the Ru-$(bpy)_3^{2+}$ that was lost in the initial laser pulse. This pattern implies that the reaction proceeds by a rate-limiting bimolecular reaction in which the ruthenium(III) complex oxidizes CrR^{2+} by one electron as in eq 5. This reaction is analogous to the reactions of organocobalt(III) macrocycles with $IrCl_6^{2-}$, in which the RCo
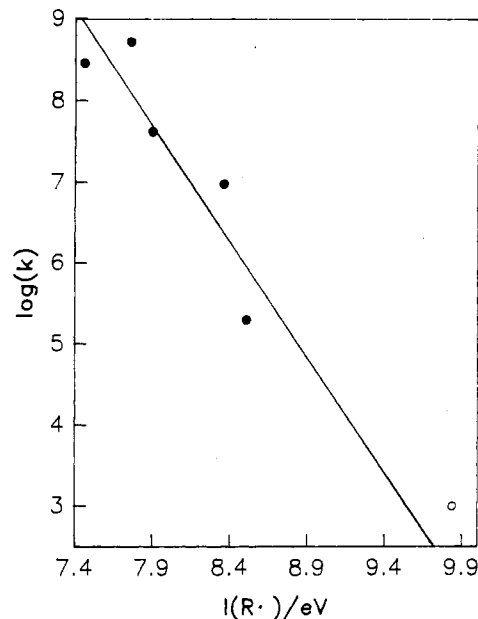

Figure 4. Dependence of the rate constant for the oxidation of CrR^{2+} complexes by $Ru(bpy)_3^{3+}$ on the ionization potential of the free radical $R^{\bullet}$. The rate constant for $R = CH_3$, for which only an upper limit was obtained, is shown as an open circle.

complexes are oxidized by one electron, eq 3.[2-4,8]

The trends in the rate constants among the complexes support the assignment of the rate-limiting step as an outer-sphere electron-transfer reaction. This is particularly evident among the alkylchromium complexes, which react in the sequence $CH_3 <<$ $CH_2CH_3 < CH(CH_3)_2$. This order is characteristic of outer-sphere electron-transfer reactions[2] in which steric effects are not very important and electronic effects predominate. Thus, addition of electron-donating methyl groups to the α-carbon of the alkyl group increases the rate of oxidation of the complex by $Ru(bpy)_3^{3+}$.

In support of the assignment of an electron-transfer mechanism, we consider the correlation of kinetic data with the ionization potential[31] of the group R bound to chromium. Figure 4 depicts the variation of $\log k$ with $IP(R^{\bullet})$ and suggests that the rate does, indeed, respond largely to this quantity. A similar reaction has been noted[2,8] for oxidation of RCo(chel) complexes by $IrCl_6^{2-}$.

Another approach to the question is to consider the variation in rate for the para-substituted benzylchromium cations. In a general sense, the replacement of para H by a ring substituent that is relatively more electron-attracting lowers the rate, as expected from the inductive effect on a reaction in which the benzylchromium cation is being oxidized. This effect can be examined quantitatively by considering the Hammett relation, which suggests a plot of $\log k_5$ vs. the substituent parameter, σ_p, as in eq 14.

$$\log k_5 = \log k_0 + \rho\sigma_p \quad (14)$$

Such a correlation does exist, although determinations were made on only four compounds.[32] The slope of this plot defines the reaction constant ρ; its value is -2.3. This compares with a value $\rho = -3.0$ for the oxidation of benzylcobaloximes by $IrCl_6^{2-}$.[2,8] The latter has been identified unequivocally as an electron-transfer reaction because it can be reversed by $IrCl_6^{3-}$ and because it gives rise to the detected cobalt(IV) intermediate $RCo(dmgH)_2^+$. The similarity of the values of the reaction constants in the two systems supports our assignement of the rate-limiting step as a reaction

(29) Actually, the apparent rate constant should be slightly higher for the quencher $(NH_3)_5Co(py)^{3+}$ since the contribution to the rate of formation of $Ru(bpy)_3^{2+}$ from eq 12, although much smaller than that from re-action between CrR^{2+} and $Ru(bpy)_3^{3+}$, is not completely negligible. A numerical simulation of the reaction scheme using the program KINSIM[30] indicated the difference should be about 3%. The slopes of the two lines in Figure 3 differ by about 13%.

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(32) The p-methylbenzyl complex deviates from the trend established by the others, but this is the least reliable value, since this complex showed deviations in the kinetic fits (see Experimental Section).

in which CrR^{2+} undergoes one-electron oxidation.

It would be desirable to consider these rates also from the standpoint of the Marcus correlation. Unfortunately, however, the necessary reduction potentials and self-exchange rates of the CrR^{3+}/CrR^{2+} couples are not yet known.

Subsequent Reactions of CrR^{3+}. The formation of an ethyl radical from the rapid unimolecular homolysis of the oxidized intermediate CrCH$_2$CH$_3$$^{3+}$ is supported by two experiments. First, the product identified by GC as ethyl bromide is readily accounted for by the reaction of the free radical with (NH$_3$)$_5$CrBr^{2+}, eq 10, for which precedents have been established. Second, the doubling of the rate constant (eq 8 vs. eq 11) noted when the quencher (NH$_3$)$_5$Co(py)$^{3+}$ is used, is consistent with the reaction of the radical with Ru(bpy)$_3$$^{3+}$, analogous to the known reaction of the radical with Ru(phen)$_3$$^{3+}$.[23]

On the other hand, we doubt that the oxidized complex CrCH$_2$OCH$_3$$^{3+}$ undergoes homolysis. More likely, it undergoes an internal electron-transfer reaction, eq 13. This is what happens when (what we presume to be) the same species is formed in the reaction with NO$^+$[14] and also by milder oxidizing agents such as Cu^{2+}, Fe^{3+}, and Hg^{2+}.[13] This mode of reaction would yield Cr$_{aq}$$^{2+}$ and CH$_3$OCH$_2$OH, and the latter would decompose to formaldehyde and methanol. Indeed, in the NO$^+$ reaction, the Cr^{2+} product of the reaction was identified and quantitatively determined.[14] In the present case the intermediate Cr^{2+} is trapped by the quencher when it is (NH$_3$)$_5$CoBr^{2+} but accumulates in preference to oxidation by Ru(bpy)$_3$$^{3+}$ when the relatively unreactive quencher (NH$_3$)$_5$Co(py)$^{3+}$ is used. In keeping with that, the rate of reduction of Ru(bpy)$_3$$^{3+}$ by CrCH$_2$OCH$_3$$^{2+}$ is very nearly[29] the same for both cobalt(III) quenching complexes.

Experimental Section

Reagents. The organochromium complexes were prepared according to the procedures described in other publications.[11–14] The complex [Co(NH$_3$)$_5$py](OSO$_2$CF$_3$)$_3$ was prepared from the reaction between pyridine (distilled from KOH) and the inner-sphere triflato-pentaammine complex. The preparation of the latter has been described in the literature.[33] Other chemicals were available from earlier work or from commercial sources.

Procedures. The laser flash photolysis system was based on one described in the literature[34] and has been detailed previously.[35] In brief,

the procedure was as follows. The photolytic excitation of Ru(bpy)$_3$$^{2+}$ was provided by a 600-ns pulse from a Phase-R Model DL-1100 dye laser (coumarin dye, emission at 460 nm) that impinged on a solution contained in a quartz fluorescence cuvette. The subsequent optical changes were monitored at right angles to the exciting pulse. The signal from the photomultiplier tube was collected by using a Nicolet digitizing oscilloscope interfaced to an Apple II+ microcomputer. A typical laser pulse kinetics experiment was performed on a solution containing [Ru(bpy)$_3$]Cl$_2$ (12–26 μM), the cobalt(III) quencher, usually [Co(NH$_3$)$_5$-Br](ClO$_4$)$_2$ (2–10 mM), and the CrR^{2+} complex (20 μM–2 mM). These solutions were maintained at ionic strength 0.10 M by addition of perchloric or hydrochloric acid. The rate constants were independent of [H$^+$] in this narrow range and were the same for Cl$^-$ and ClO$_4$$^-$ solutions. The transmittance data, converted to absorbance values that, with one exception, followed first-order kinetics for 3 half-lives. For reasons not ascertained, the reaction of the complex CrCH$_2$C$_6$H$_4$-p-CH$_3$$^{2+}$ followed biphasic kinetics, which were deconvoluted by standard methods. The first (faster) reaction responds to the proper concentration variables and is presumed to be the process of interest.

The analysis for the organic product(s) of the reaction between Ru(bpy)$_3$$^{3+}$ and CrCH$_2$CH$_3$$^{2+}$ was carried out. This was done in an experiment in which the Ru(III) complex was generated by continuous photolysis of a stirred solution containing Ru(bpy)$_3$$^{2+}$ (56 μM), (NH$_3$)$_5$CoBr^{2+} (0.01 M), and CrCH$_2$CH$_3$$^{2+}$ (5.0 mM) in a cell having a jacket containing 0.01 M (NH$_3$)$_5$CoBr^{2+} (to act as a filter of the UV light so that the products derived from photolysis of the ruthenium complex, not the cobalt quencher). The cell was irradiated for 4 min with a 275-W sunlamp placed 14 cm away. After a sufficient time (4 h) for the remaining ethylchromium(2+) ion to decompose to ethane by acidolysis, the reaction mixture was analyzed by gas chromatography on a 10% FFAP column. The result, in comparison with standards, established the only organic product to be ethyl bromide.

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Characterization of the Structure, Properties, and Reactivity of a Cobalt(II) Macrocyclic Complex

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The cobalt(II) macrocycle L$_2$Co(dmgBF$_2$)$_2$ has been characterized by crystallography (L = CH$_3$OH) and by spectroscopic UV/vis, EPR, electrochemical, and magnetic methods as well as elemental analysis for L = H$_2$O. The complex (CH$_3$OH)$_2$Co(dmgBF$_2$)$_2$ crystallizes in the triclinic space group P$\bar{1}$ with one molecule in a cell of dimensions a = 7.955 (6) Å, b = 8.180 (6) Å, c = 7.918 (6) Å, α = 99.55 (2)°, β = 118.13 (2)°, and γ = 66.52 (2)°. The data refined to a final value of the weighted R factor of 0.046 based on 1027 independent observations. It is a six-coordinate, low-spin complex (μ = 1.92 μ_B), showing substantial elongation of the axial Co–O bonds (2.27 Å). In aqueous perchloric acid the diaquo complex is reversibly oxidized to (H$_2$O)$_2$Co(dmgBF$_2$)$_2$$^+$ by Fe^{3+}. The equilibrium constant is 34.7 (25 °C), yielding $E°$ = 0.65 V vs. NHE for the Co(III)/Co(II) couple. The second-order rate constant for the forward reaction has the value k_f/M^{-1} s^{-1} = 2.9 × 10^2 + 1.2 × 10^2[H$^+$]$^{-1}$. The prominent inverse-[H$^+$] component suggests an inner-sphere reaction between (H$_2$O)$_5$FeOH^{2+} and the Co(II) complex. A detailed analysis of the mechanism interpreted on that basis is presented; it suggests that intramolecular electron transfer within a binuclear intermediate is the rate-limiting step.

Introduction

In spite of extensive earlier investigations, complexes of cobalt with macrocyclic ligands continue to be actively studied. They hold continued interest not only because of their relationship to

the intriguing chemistry of vitamin B$_{12}$,[1–3] but also because they offer a wide variety of chemistry within a family of well-defined

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