spectra confirm the compounds. The C=O stretching vibration, 1837 (**15**) and 1836 cm^{-1} (**16**), is found in the typical region for fluorinated chloroformates. The ^{19}F NMR spectra of **15** and **13** as well as **16** and **14** are almost identical in shift values and coupling constants.

The reaction with sulfur dioxide, however, does not yield the expected chlorosulfates (eq 22). In both cases **13** and **14** are

$$\underset{\mathbf{13,\ 14}}{ClOCF_2CFXSO_2F} + SO_2 \not\rightarrow ClSO_2OCF_2CFXSO_2F \qquad (22)$$

catalytically decomposed by SO_2 according to (eq 23). This result is thus identical to that of the photolysis reactions.

$$\underset{\mathbf{13,\ 14}}{ClOCF_2CFXSO_2F} \xrightarrow{(SO_2)} ClCFXSO_2F + COF_2 \qquad (23)$$

Summary

Improved methods for preparing the known salts $MOCF_2CF(X)SO_2F$ (X = F, CF_3) have been developed. The instability of the salt $MOCF_2CF(CF_3)SO_2F$ in the presence of fluoride ion in polar solvents was demonstrated, and the complex reactions leading to formation of stabilized complex of KF with $O{=}C{=}C(CF_3)C(O)C_2F_5$ were fully characterized. The new hypochlorites $ClOCF_2CF(X)SO_2F$ were prepared by reactions of ClF or $ClOSO_2F$ with the respective metal salts and fully characterized. Unexpected thermal stability of $ClOCF_2CF(CF_3)SO_2F$ compared to previously known hypochlorites of related structure was found, and the stabilizing effect of the $-SO_2F$ group in both hypochlorites was evident. The reactivity of the O–Cl bonds with CO to form chloroformates was as expected, but reactions with SO_2 led to a catalytic decomposition with loss of COF_2.

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Registry No. **1**, 697-18-7; **2**, 1858-59-9; **3**, 773-15-9; **4**, 677-67-8; **5**, 754-41-6; **6**, 81439-24-9; **7**, 136490-29-4; **8**, 136490-30-7; **9**, 136490-31-8; **10**, 94560-03-9; **11**, 53352-88-8; **12**, 41874-82-2; **13**, 136490-32-9; **14**, 136490-33-0; **15**, 136490-34-1; **16**, 136490-35-2; $ClCF_2SO_2F$, 64544-26-9; $CF_3CF{=}CF_2$, 116-15-4; SO_3, 7446-11-9; $C_2F_5C(O)F$, 422-61-7; $CF_3CHFC(O)F$, 6065-84-5; CF_3CHFSO_2F, 2127-74-4; $CF_3CF(Cl)SO_2F$, 25221-40-3.

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Alkyl Radical Colligation and Release by a Chromium Macrocycle

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Alkyl radicals, generated from the photohomolysis of organocobalt complexes, were allowed to react in aqueous solution with $(H_2O)_2CrL^{2+}$ (L = 1,4,8,12-tetraazacyclopentadecane or [15]aneN_4). The reaction rates were evaluated by laser flash photolysis, using the known reaction between R$^•$ and the methyl viologen radical cation as a kinetic probe. Data were obtained for reactions of 13 radicals. The rate constants span a narrow range, (6–19) × 10^7 L mol^{-1} s^{-1} at 25 °C. The decomposition of $CH_3CH(OH)CrL(H_2O)^{2+}$ takes place by concurrent homolysis and β-elimination. At 25 °C the overall rate constant has a value (1.60 ± 0.15) × 10^{-4} s^{-1} independent of [H^+]. The complexes with R = CH_2OH and CH_2OCH_3 undergo decomposition too slowly for detection. Equilibrium constants for radical binding calculated from forward and reverse rate constants are log K_{298} = 11.23 ($CH(CH_3)_2$) and 12.19 ($CH_2C_6H_5$). The kinetic and equilibrium data are discussed in terms of a reaction model featuring concurrent Cr–C and Cr–OH_2 bond making and bond breaking. Results for analogous reactions are compared.

Introduction

Colligation[1] reactions between free radicals and certain transition-metal complexes lead to the formation of stable metal–carbon bonds: $ML_{n+1} + R^• \rightarrow L_nMR + L$. The resulting complexes are stable with respect to the reverse reaction, dissociation of a free radical, unless forced to completion by the addition of a radical trap. Isolated cases of colligation reactions of alkyl radicals have been investigated.[2-6] These often involve $^•CH_3$, because it is easily generated pulse radiolytically by the reaction of HO$^•$ with $(CH_3)_2SO$. More recently, systematic investigations of the kinetics of colligation reactions have been reported. Data are now available[7-10] for $Cr(H_2O)_6^{2+}$, Vitamin B_{12r}, cobalt(II) complexes of N_4 macrocycles such as [14]aneN_4 (=1,4,8,11-tetraazacyclotetradecane), and the nickel(II) complexes *RRSS*-Ni([14]aneN_4)$^{2+}$ and *RRRR*-Ni([14]aneN_4)$^{2+}$. The reactions of this group of complexes have been examined for quite a range of primary and secondary alkyl and substituted alkyl radicals. This work has been facilitated because alkyl radicals can be produced by the laser flash photolysis of organocobalt complexes. Kinetic probes have been used to monitor the reaction progress, since the attendant absorbance changes are otherwise too small for observation.

We turn our attention here to reactions of the chromium complex of the macrocycle [15]aneN_4, or 1,4,8,12-tetraazacyclopentadecane = L. The organometallic complexes RCr([15]aneN_4)$(H_2O)^{2+}$ were originally prepared[11] by reduction of alkyl halides by the chromium(II) macrocycle (eq 1 and 2). The structure of one compound was recently determined crystallographically for R = 4-$BrC_6H_4CH_2$.[12]

$$(H_2O)_2CrL^{2+} + RX \rightarrow XCrL(H_2O)^{2+} + R^• + H_2O \qquad (1)$$

$$(H_2O)_2CrL^{2+} + R^• \rightarrow RCrL(H_2O)^{2+} + H_2O \qquad (2)$$

In this sequence, eq 1 is rate controlling. Study of the much faster second reaction requires the sudden generation of the radical in a solution containing $(H_2O)_2CrL^{2+}$. Pulse radiolysis was used[13]

(1) "The process of forming a covalent bond by means of one electron of each of the combining units will be called *colligation*. ...It is to be distinguished from co-ordination ... the distinction is in the process by which the bond is formed, not in the bond itself." Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1969; p 5.
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Table I. UV-Visible Spectra of $RCr([15]aneN_4)H_2O^{2+}$ Complexes in Acidic Aqueous Solution

R	λ_{max}/nm (ϵ/L mol^{-1} cm^{-1})		
CH_2OH	270 (1030 ± 100)	377 (200 ± 10)	450 (55 ± 3)
$CH(CH_3)OH$	320 (650 ± 60, sh)	383 (203 ± 15)	458 (50 ± 8)
CH_2OCH_3		377 (220 ± 25)	450 (68 ± 15)

to evaluate the rate constant of eq 2 for R = CH_2OH and $C(CH_3)_2OH$. Here we have used laser flash photolysis to study eq 2 for a wide range of alkyl radicals.

Colligation reactions of alkyl radicals and metal complexes studied to date divide cleanly into two groups. The first group includes $Cr(H_2O)_6^{2+}$ and $Co(N_4mac)^{2+}$, where the rates decrease relatively little as the substituents on the α-carbon atom increase in bulk. In contrast, the second group, which includes both isomers of $Ni([14]aneN_4)^{2+}$, shows rates that decrease markedly with the size of the substituents. Rationale for this difference includes a consideration of structural factors.[9,10] The macrocyclic chromium complexes promise to offer some interesting comparisons, since their chemical reactivities[14] do not entirely parallel those of the $(H_2O)_5CrR^{2+}$ analogues. In particular we seek to learn whether incorporation of the chromium into a macrocycle causes its reactivity pattern to shift to that of the nickel macrocycles.

We have also examined the reactivity of the complex $CH_3CH(OH)CrL(H_2O)^{2+}$. We chose this complex because the pentaaqua complex provides a clear balance between heterolysis and homolysis and because the aliphatic radical derived from it is sufficiently reducing as to be readily trapped by cobalt(III) complexes.

Experimental Section

Materials. The laboratory distilled, deionized water was passed through a Millipore-Q purification system. The organometallic complexes $RCo(dmgH)_2OH_2$ and $RCo(dmgH)_2py$ were prepared as in the literature,[15] as were the complexes $RCo([14]aneN_4)OH_2^{2+}$ (R = CH_3, C_2H_5, CH_2Br, CH_3OCH_2).[16] Chromium(II) chloride[17] was used to synthesize $(H_2O)_2Cr([15]aneN_4)^{2+}$ in solution upon anaerobic addition of an equimolar quantity of 1,4,8,12-tetraazacyclopentadecane. Such solutions, appropriately diluted under rigorously anaerobic conditions, were used directly for kinetics studies. In the preparation of $RCrL(H_2O)^{2+}$ complexes (R = CH_2OH, $CH_3CH(OH)$, CH_2OCH_3), a solution of $(H_2O)_2CrL^{2+}$, ~0.05 M, was treated with CH_3OH, C_2H_5OH, or $(CH_3)_2O$, typically 0.5 M, followed by a slightly less than stoichiometric amount of H_2O_2. The resulting brown solution was acidified to pH 1 and placed on an oxygen-free, ice-water-cooled column of Sephadex C25 resin, from which the desired yellow-orange complex was eluted with 0.15 M $HClO_4$. UV–visible spectra of these complexes are given in Table I. The same reaction with $(CH_3)_2CHOH$ failed to yield $(CH_3)_2C(OH)CrL(H_2O)^{2+}$, presumably because it undergoes homolysis too rapidly.

Methyl viologen dichloride hydrate was recrystallized twice from methanol. Stock solutions were protected from light and oxygen. As needed, solutions of the persistent $MV^{\bullet+}$ radical were prepared by reduction over amalgamated zinc. They were handled and transferred strictly anaerobically and were not stored for long.

Analyses. Organochromium complexes were oxidized with alkaline peroxide, and the chromium content was determined spectrophotometrically as chromate at 372 nm.[18] Reproducible results required prior decomposition of the organochromium complex by strongly heating with concentrated perchloric acid (*caution!*) before the alkaline peroxide step. Cobalt(II) was determined as $Co(NCS)_4^{2-}$ at 623 nm (ϵ 1842 L mol^{-1} cm^{-1}) in 50% aqueous acetone.[19]

Acetaldehyde was determined gas chromatographically on an OV101 column at 30 °C. Calibration curves were constructed using standard solutions cooled in ice to prevent loss of CH_3CHO by volatilization. A blank experiment showed that no acetaldehyde was present in the preparation of the organochromium complex with R = $CH(CH_3)OH$. Although acetaldehyde could be found when a solution of freshly prepared organochromium complex was injected, it was presumably produced at the injection port, since none was present in the gas phase.

The test for H_2 as a decomposition product of $CH_3CH(OH)CrL(H_2O)^{2+}$ was carried out on a scale approximately five times that of the kinetic runs. The test was carried out by very slowly purging the reaction mixture with argon and bubbling the outlet gas through a dilute solution of $PdCl_2$ (~0.02 M) in 0.01 M $HClO_4$.

Kinetics. The homolysis rate of $CH_3CH(OH)CrL(H_2O)^{2+}$ was determined spectrophotometrically. The solution contained excess $Co(NH_3)_5Cl^{2+}$ to draw the reaction to completion. The loss of the complex was monitored at 320 and 383 nm. The reaction temperature, [H^+], and ionic strength were precisely controlled.

Colligation rates were measured by laser flash photolysis. The source of $R^\bullet$ was $RCo(dmgH)_2H_2O$ and $RCo([14]aneN_4)H_2O^{2+}$. The dye laser used Coumarin 460 or LD 490. Temperature control was maintained in the reaction cell by circulation of thermostated water through the wall of the cell holder. The absorbance changes accompanying the reaction of interest were too small to permit monitoring at the relatively low concentrations of $RCrL(H_2O)^{2+}$ produced in the 0.6-μs pulse width of the laser. Thus the reaction was studied by using the methyl viologen radical cation as a kinetic probe. The loss in $MV^{\bullet+}$ was monitored at 600 nm (ϵ 1.37 × 10^4 L mol^{-1} cm^{-1}).[20]

The three reactions occurring are given in eqs 3–5, which show that the radical can undergo self-reactions, addition to $MV^{\bullet+}$, and colligation with the chromium(II) complex.

$$2R\bullet \rightarrow R_2\ (+RH + R_{-H})\quad (k_d) \tag{3}$$

$$R^\bullet + MV^{\bullet+} \rightarrow RMV^+\quad (k_{MV}) \tag{4}$$

$$R^\bullet + (H_2O)_2CrL^{2+} \rightarrow RCrL(H_2O)^{2+} + H_2O\quad (k_{col}) \tag{5}$$

If chromium is absent, the rate of reaction is as shown in eq 6. As

$$-d[R^\bullet]/dt = 2k_d[R^\bullet]^2 + k_{MV}[R^\bullet][MV^{\bullet+}] \tag{6}$$

$$k_\psi = 2k_d[R^\bullet]_{av} + k_{MV}[MV^{\bullet+}] \tag{7}$$

explained before,[7,8,21] eq 6 can be approximated as a first-order kinetic expression (eq 7), since the concentration of $R^\bullet$ is so low ((2–5) × 10^{-6} M) that it contributes a small but not negligible amount to k_ψ (5% is typical).

With $(H_2O)_2CrL^{2+}$ added, the observed rate constant $k_{\psi,Cr}$ contains an additional term, $k_{col}[(H_2O)_2CrL^{2+}]$. Since the constants of eq 7 are known,[7,21,22] the dependence of $k_{\psi,Cr}$ on chromium concentration can be analyzed in terms of a corrected rate constant as in eq 8.

$$k_{corr} = k_{\psi,Cr} - 2k_d[R^\bullet]_{av} - k_{MV}[MV^{\bullet+}] = k_{col}[(H_2O)_2CrL^{2+}] \tag{8}$$

A value of [$MV^{\bullet+}$] is determined for each experiment from the absorbance at 600 nm. An estimate of the average radical concentration, $[R^\bullet]_0/2$, is needed. The value was calculated according to eq 9 and

$$[R^\bullet]_{av} = \frac{\Delta[MV^{\bullet+}]k_\psi}{2k_{MV}[MV^{\bullet+}]_{av}} \tag{9}$$

refined iteratively if necessary. The relation[21] in eq 9 derives from the fact that the fraction of the radical that reacts with MV^+, $\Delta[MV^+]/[R]_{tot}$, equals $k_{MV}[MV^{\bullet+}]/k_\psi$.

The validity of eqs 6–9, including the approximation to first-order kinetics, was checked by the use of concentrations calculated by numerical integration of the differential equation, which was done with the program KINSIM.[23]

Results

Decomposition reactions were examined for $RCrL(H_2O)^{2+}$, for R = CH_2OH, CH_2OCH_3, and $CH(CH_3)OH$. The complexes with R = CH_2OH and CH_2OCH_3 are quite stable, showing negligible changes in their spectra over more than 6 h in acidic solution under argon. The complex with R = $CH(CH_3)OH$ undergoes a first-order decomposition reaction in the presence of a scavenger such as $Co(NH_3)_5Cl^{2+}$. This cobalt complex was chosen to establish whether the decomposition occurs by homolysis (eq 10), because

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$$CH_3CH(OH)CrL(H_2O)^{2+} \xrightarrow{H_2O} (H_2O)_2CrL^{2+} + {}^{\bullet}CH(CH_3)OH \quad (10)$$

$${}^{\bullet}CH(CH_3)OH + Co(NH_3)_5Cl^{2+} \xrightarrow{H^+} CH_3CHO + Cl^- + Co^{2+} + 5NH_4^+ \quad (11)$$

$$(H_2O)_2CrL^{2+} + Co(NH_3)_5Cl^{2+} \xrightarrow{H^+} (H_2O)CrL(Cl)^{2+} + Co^{2+} + 5NH_4^+ \quad (12)$$

$Co(NH_3)_5Cl^{2+}$ is known to react with $^{\bullet}CH(CH_3)OH$ (eq 11, $k = 3.0 \times 10^6$ L mol^{-1} s^{-1}).[24] Also the chromium(II) complex is expected to reduce $Co(NH_3)_5Cl^{2+}$ rapidly (eq 12), because $Cr(H_2O)_6^{2+}$ does so ($k = 2.6 \times 10^6$ L mol^{-1} s^{-1}).[25]

The kinetics were studied in 0.10 M perchloric acid, ionic strength being maintained at 1.0 M with sodium perchlorate. The reactant concentration was typically 2–3 mM, and $[Co(NH_3)_5Cl^{2+}]$ was varied in the range 6–16 mM. The decrease in the concentration of the organochromium complex was monitored at 320 and 383 nm. The rate constant, $k = (1.60 \pm 0.15) \times 10^{-4}$ s^{-1} at 25.0 °C, is independent of cobalt concentration as expected from the sequence in eqs 10–12 and independent of $[H^+]$ in the range 0.10–1.0 M. When no cobalt scavenger was added, an absorbance decrease occurred at about the same rate, but the data did not fit as cleanly to first-order kinetics.

The rate constants were evaluated as a function of temperature with values of $k/10^{-4}$ s^{-1} (T/°C) as follows: 0.61 (20.2), 1.55 (24.8), 2.25 (29.7), 5.79 (34.5), and 9.80 (39.5). These values were not analyzed according to the equation from activated complex theory, because the rate constant is, as presented in the Discussion, a composite of two and likely three parallel reactions.

The yields of acetaldehyde and Co^{2+} were determined on solutions in which the decomposition of $CH_3CH(OH)CrL(H_2O)^{2+}$ was allowed to go to completion. The value of $[CH_3CHO]_\infty/[RCrL(H_2O)^{2+}]_0$ was 0.52 ± 0.08 in the absence of cobalt and 0.82 ± 0.09 when 8.8 mM $Co(NH_3)_5Cl^{2+}$ was present in a solution of 3.5 mM organochromium complex and 0.16 M perchloric acid. The same solutions gave $[Co^{2+}]_\infty/[RCrL(H_2O)^{2+}]_0 = 0.56 \pm 0.04$. This ratio, unlike the kinetic data, depends also on cobalt and acid concentrations. Yields of Co^{2+} increase at higher $Co(NH_3)_5Cl^{2+}$ concentrations and lower acid concentrations. In 0.058 M $HClO_4$ with 10.1 mM $Co(NH_3)_5Cl^{2+}$ the ratio $[Co^{2+}]_\infty/[RCrL(H_2O)^{2+}]_0 = 1.76$. Also, in the absence of cobalt, H_2 was detected as a product of decomposition by the test with palladium chloride.[26] However, with excess cobalt present no H_2 was detected.

Reactions of Alkyl Radicals: Colligation. Solutions containing the organocobalt complex (the radical precursor), the methyl viologen radical cation, and sometimes $(H_2O)_2CrL^{2+}$ were subjected to a single-shot laser flash. The absorbance was monitored at 600 nm to record the decrease in concentration of $MV^{\bullet+}$. When the chromium complex was absent, the value of k_ψ varied linearly with $[MV^{\bullet+}]$, as expected from eq 7. The slope of the line for each radical gives the value of the rate constant for its reaction with $MV^{\bullet+}$. The values of k_{MV} so obtained are given in Table II; they agree with previous determinations, where available.

In the reaction with $(H_2O)_2CrL^{2+}$, it was essential that the organocobaloxime be freshly purified. Any trace amount of inorganic cobalt such as $Co(dmgH)_2^+$ resulted in the formation of H_2, identified by the test with palladium chloride.[26] The H_2 was presumably formed by the cobalt-catalyzed reduction of H^+ by $(H_2O)_2CrL^{2+}$, analogous to the known cobalt-catalyzed reaction of H^+ and $Cr(H_2O)_6^{2+}$.[27]

When a mixture of $RCo(dmgH)_2H_2O$, $MV^{\bullet+}$, and $(H_2O)_2CrL^{2+}$ is subjected to the 490-nm laser flash, the absorbance of $MV^{\bullet+}$ at 600 nm again decreases with time. Now, however, with the chromium(II) complex present the absorbance decrease is smaller and the rate is higher. At a given concentration

Table II. Rate Constants[a] for the Reactions of Alkyl and Substituted Alkyl Radicals with the Methyl Viologen Radical Ion and with $(H_2O)_2Cr([15]aneN_4)^{2+}$

radical	$k_{MV}/10^9$ L mol^{-1} s^{-1}	$k_{col}/10^7$ L mol^{-1} s^{-1}
CH_3	1.5 ± 0.4	16 ± 1
		19 ± 2[b]
CH_2CH_3	1.0 ± 0.1	10 ± 1
		9.5 ± 0.2[b]
$CH_2C_2H_5$	1.0 ± 0.1	8.5 ± 0.4
$CH(CH_3)_2$	1.2 ± 0.1	6.1 ± 0.3
$CH_2C_3H_7$	1.2 ± 0.1	8.2 ± 0.5
$CH(CH_3)C_2H_5$	1.1 ± 0.1	3.9 ± 0.4
$CH_2CH(CH_3)_2$	0.92 ± 0.09	7.3 ± 0.2
c-C_5H_9	0.91 ± 0.09	7.1 ± 0.4
$CH_2C(CH_3)_3$	0.76 ± 0.08	6.3 ± 0.2
CH_2OCH_3	1.1 ± 0.1	16 ± 1
		14 ± 1[b]
CH_2Cl	1.1 ± 0.2	9.3 ± 0.7
CH_2Br	1.5 ± 0.1	13 ± 1
		16 ± 1[b]
CH_2Ph	1.2 ± 0.1	19 ± 1

[a] At 25 ± 1 °C, $[R^\bullet] \sim 1$–4 μM, $[MV^{\bullet+}] = (1$–$8) \times 10^{-5}$ M, with $RCo(dmgH)_2H_2O$ as the radical sources except as noted. [b] With $RCo([14]aneN_4)H_2O^{2+}$ as the radical source.

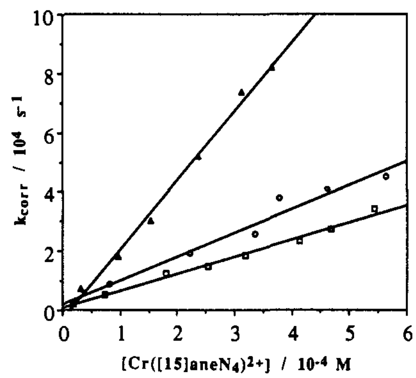

Figure 1. Observed pseudo-first-order rate constants, corrected for radical self-reactions and the reaction of $R^\bullet$ with $MV^{\bullet+}$, varying linearly with $[(H_2O)_2CrL^{2+}]$. Data at 25.0 °C are shown for the reactions of $C_6H_5CH_2^\bullet$ (triangles), 1-$C_4H_9^\bullet$ (circles), and $^{\bullet}CH(CH_3)C_2H_5$ (squares).

of $MV^{\bullet+}$, the value of $k_{\psi,Cr}$ increases with $[(H_2O)_2CrL^{2+}]$. To accommodate data taken over a range of $MV^{\bullet+}$ concentrations, the values of $k_{\psi,Cr}$ were corrected for the radical self-reaction and the $MV^{\bullet+}$ reaction. The values of k_{corr}, calculated as in eq 8, vary linearly with $[(H_2O)_2CrL^{2+}]$. Data are shown in Figure 1 for $R^\bullet = C_6H_5CH_2$, 1-C_4H_9, and 2-C_4H_9. These plots pass approximately through the origin, as expected from the model proposed. The slopes of these lines are the rate constants for the colligation reaction between $R^\bullet$ and $(H_2O)_2CrL^{2+}$, k_{col}. The values of k_{col} at 25.0 °C are summarized in Table II. The errors assigned to each of the values represent one standard deviation of the least-squares fit of values of k_{corr} as a function of $[(H_2O)_2CrL^{2+}]$, as in eq 8. Given that k_{corr} itself is the difference between the experimental rate constant and that calculated for two other reactions, the actual uncertainties in k_{col} may be larger, probably of the order of 10–15%.

Discussion

Decomposition Reactions. The modified Fenton reaction between $Cr(H_2O)_6^{2+}$ and H_2O_2 in the presence of a suitable aliphatic substrate RH has proved to be a successful method for the preparation of $(H_2O)_5CrR^{2+}$ complexes.[28-30] The same method was used here to prepare macrocyclic analogues with R =

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CH_2OH, $CH(CH_3)OH$, and CH_2OCH_3, but it failed for R = $C(CH_3)_2OH$. We suggest that this is due to the homolysis of $(CH_3)_2C(OH)Cr([15]aneN_4)H_2O^{2+}$ being too rapid, which is not unreasonable in view of the fact that the pentaaqua analogue decomposes with $k_{hom} = 0.13\ s^{-1}$ ($t_{1/2} = 5.5$ s) at 25 °C.[30]

The complex $RCrL(H_2O)^{2+}$ with R = CH_2OH does not decompose by homolysis. This is not unexpected, since $(H_2O)_5CrCH_2OH^{2+}$ does so only slowly. However, the fact that complexes with R = CH_2OH and CH_2OCH_3 do not undergo acidolysis contrasts with the behavior of the $(H_2O)_5CrR^{2+}$ analogues, which do so readily (R = CH_2OH) or slowly (R = CH_2OCH_3).[30,31] The failure of the acidolysis reaction for the macrocyclic complexes is precedented, however, in that the 1-propyl and 2-propyl macrocyclic complexes are completely stable toward acidolysis under conditions where their pentaaqua counterparts readily react.[12] This contrast in reactivity is particularly striking, because the N_4 macrocycle, a good electron-donating ligand, might be expected to increase the rate of electrophilic attack by virtue of its inductive effect. The lack of acidolysis may be further indication that electrophilic attack by water arises from the internal attack of cis-coordinated water in the $(H_2O)_5CrR^{2+}$ series of complexes, which cannot happen in the macrocycle. Earlier studies of organochromium complexes containing edta and nitriloacetate ligands[13,32] gave acidolysis rates that were similar, for the H_2O pathway, to those found in the pentaaqua series. These authors[13] also found that $CH_3CH(OH)CrL(H_2O)^{2+}$ does not undergo acidolysis with H_2O or H_3O^+. They argued, however, that the similarity of rates for $(H_2O)_5$, edta, and nta complexes signaled the same mechanism for the H_2O path—attack of an external, noncoordinated water molecule. Evidently the basis for this is that the edta complex, which lacks a cis-coordinated water, reacts similarly to the others. We suggest that the really striking feature is the failure of the $[15]aneN_4$ complexes to react at all. Perhaps the edta complex can, by hydrogen bonding, utilize a water molecule in the second coordination sphere.[13,32]

The extreme slowness of electrophilic attack of H_3O^+ on the macrocycles might therefore indicate the difficulty the small H_3O^+ electrophile experiences in approaching the α-carbon atom by virtue of repulsion from the ligand. Larger electrophiles (Hg^{2+}, Br_2, I_2) evidently do not show this effect, since these displacement reactions occur rapidly and readily.[12,33]

On the basis of eq 10, 14, and 15, the expected yield of acetaldehyde in the absence of a radical scavenger is 0.2, given that

$$CH_3CH(OH)CrL(H_2O)^{2+} \xrightleftharpoons{H_2O} (H_2O)_2CrL^{2+} + {}^{\bullet}CH(CH_3)OH \quad (13)$$

$$2{}^{\bullet}CH(CH_3)OH \rightarrow CH_3CHO + CH_3CH_2OH \quad (14)$$

$$2{}^{\bullet}CH(CH_3)OH \rightarrow CH_3CH(OH)CH(OH)CH_3 \quad (15)$$

$${}^{\bullet}CH(CH_3)OH + CH_3CH(OH)CrL(H_2O)^{2+} \rightarrow CH_3CHO + CH_3CH_2OH + (H_2O)_2CrL^{2+} \quad (16)$$

$$CH_3CH(OH)CrL(H_2O)^{2+} \rightarrow CH_3CHO + HCrL(H_2O)^{2+} \quad (17)$$

$$HCrL(H_2O)^{2+} + H_3O^+ \rightarrow (H_2O)_2CrL^{3+} + H_2 \quad (18)$$

$$HCrL(H_2O)^{2+} + 2Co(NH_3)_5Cl^{2+} \xrightarrow{H^+} (H_2O)CrL(Cl)^{2+} + 2Co^{2+} + 10NH_4^+ + Cl^- \quad (19)$$

$k_{14} = 1.1 \times 10^8$ and $k_{15} = 5.5 \times 10^8\ L\ mol^{-1}\ s^{-1}$.[34,35] To account for a yield of acetaldehyde that approaches 0.5, an additional reaction (eq 16 or 17) is proposed. Precedent for eq 16 can be found in the reaction between $(H_2O)_5CrCH(CH_3)_2^{2+}$ and hydrogen peroxide[36] and in the pulse-radiolytic study of the homolysis of $(H_2O)_5CrR^{2+}$ complexes.[37] The latter study suggested that rate constants for reactions of $R^{\bullet}$ with CrR^{2+} can exceed $10^8\ L\ mol^{-1}\ s^{-1}$. If k_{16} has such a value, then the observed yield of CH_3CHO (0.5) might be explained. However, a very valid objection can be raised to eq 16 in this case. Upon the occurrence of reaction 16, a second organochromium is lost. If eq 16 were the dominant path, the k_{obs} would be $2k_{hom}$. That is, the experimental rate constant would be expected to drift by up to a factor of 2 as the reaction conditions and concentrations varied, which was not found experimentally.

We therefore consider eq 17, a β-elimination reaction. This sort of chemistry is well precedented elsewhere in organometallic chemistry. It would also account for the extra acetaldehyde, if β-elimination occurs concurrently with homolysis. As such, eq 17 would not lead to the kinetic problems raised by eq 16. The pentaaqua analogue of the hydrido complex shown as a product is known independently[38,39] to evolve hydrogen under these conditions (eq 18). Indeed, H_2 was observed as a product of decomposition of $CH_3CH(OH)CrL(H_2O)^{2+}$.

In the presence of a scavenger such as $Co(NH_3)_5Cl^{2+}$ additional reactions occur, such as those shown in eqs 11, 12, and 19. The yield of acetaldehyde in the presence of $Co(NH_3)_5Cl^{2+}$ was found to be higher (0.82) than in its absence, indicating Cr–C bond homolysis is also occurring. This is still lower than the expected acetaldehyde yield of 1 in the presence of $Co(NH_3)_5Cl^{2+}$, indicating that acidolysis of $CH_3CH(OH)CrLH_2O^{2+}$ may be occurring to a minor extent or simply that some acetaldehyde is lost despite cooling the solution in ice.

The predicted yield of Co^{2+} is 2.0 on the basis of eqs 11 and 12 if homolysis predominates. However, in 0.16 M $HClO_4$ the yield was only 0.56 ($[Co^{2+}]_\infty/[RCrL(H_2O)^{2+}]_0$). This indicates that, at most, 28% of the organochromium complex decomposes by homolysis. Also, the Co^{2+} yield was found to be higher at lower acid concentration and to depend on $Co(NH_3)_5Cl^{2+}$ concentration. This is understood in terms of eqs 18 and 19. As cobalt concentration is increased, more hydrido complex reacts as in eq 19 and yields of Co^{2+} increase. At low $[H^+]$ and the highest cobalt concentration of 10.1 mM, a yield of $[Co^{2+}]_\infty/[RCrL(H_2O)^{2+}]_0 = 1.76$ was obtained. This is again slightly less than the expected yield, and the small discrepancy may be due to eq 18 or to a small contribution by acidolysis.

To summarize, the product studies indicate that a significant portion of the decomposition of $CH_3CH(OH)CrL(H_2O)^{2+}$ is β-elimination. The remainder may be homolysis; however, a small ($\leq$18%) contribution by acidolysis cannot be ruled out. This is similar to the case of isobutylcobalamin in which β-elimination and Co–C bond homolysis are competitive processes.[40]

Colligation Reactions. The rate constants k_{MV}, referring to eq 4, were previously determined for many of these same radicals.[7] The values found here all agree within the experimental error; indeed, they were redetermined only because the subtraction inherent in the evaluation of k_{col} (see eq 8) requires accurate values under precisely the same conditions. There are two factors that combine to make $MV^{\bullet+}$ an ideal probe for the reactions of alkyl radicals—the high values of k_{MV} and the high molar absorptivity of $MV^{\bullet+}$, which allow the use of low concentrations of $MV^{\bullet+}$ and the monitoring of an appreciable absorbance change.

The values of k_{col}, referring to the reactions of $R^{\bullet}$ with $(H_2O)_2CrL^{2+}$, lie in a relatively narrow range, from 3.9 to $10^7\ L\ mol^{-1}\ s^{-1}$ for $R^{\bullet}$ = 1-methylpropyl to $1.9 \times 10^8\ L\ mol^{-1}\ s^{-1}$ for benzyl. If one searches for a steric effect, reflected in the values of k_{col}, such as in a series like ${}^{\bullet}CH_3$, ${}^{\bullet}C_2H_5$, and ${}^{\bullet}CH(CH_3)_2$, it is largely absent. In the case of $Cr(H_2O)_6^{2+}$, also no steric effect was found,[7,29] with values of k_{col} all near $2 \times 10^8\ L\ mol^{-1}\ s^{-1}$. The small reduction in rates in going from $Cr(H_2O)_6^{2+}$ to $(H_2O)_2CrL^{2+}$ may perhaps be attributed to a statistical effect (six vs two replaceable water molecules) or to the macrocycle partially blocking the approach of $R^{\bullet}$. If this reaction, in which chromium(II) is oxidized, were really of an electron-transfer character one might

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Table III. Values of Rate Constants and Equilibrium Constants for $RCr([15]aneN_4)(H_2O)^{2+}$ Complexes in H_2O at 25 °C

R	$k_{col}/10^7$ L mol^{-1} s^{-1}	$k_{hom}/10^{-4}$ s^{-1} [a]	log (K/L mol^{-1})
$^•CH(CH_3)_2$	8.5	5.0	11.23
$^•CH_2C_6H_5$	19	1.24	12.19

[a] Reference 14.

Table IV. Values of log K for Organochromium and Organonickel Complexes

R	$(H_2O)_2$-CrL^{2+}	Cr-$(H_2O)_6^{2+}$ [a]	*RRRR*-$[Ni([14]aneN_4)^{2+}]$ [b]
$^•CH(CH_3)_2$	11.23	11.87	3.49
$^•CH_2C_6H_5$	12.19	10.52	
$^•CH(CH_3)OH$		10.96	
$^•CH_2OCH_3$		>13.8	6.82

[a] References 7, 13, and 14. [b] Reference 10.

have expected a faster reaction of the macrocyclic complex, since it is the better reducing agent ($E° = -0.58$ V vs -0.41 V for $Cr(H_2O)_6^{2+}$).

An important point is that the analogous reactions of the $Ni([14]aneN_4)^{2+}$ complexes *do* show a significant rate reduction along the series $^•CH_3 > {}^•C_2H_5 > {}^•CH(CH_3)_2$. The present results show that this cannot be attributed to an effect of the macrocycle. As suggested before,[9,10] the large reactivity ratios in the case of $Ni([14]aneN_4)^{2+}$ are due to the change in coordination number and the fact that the organonickel complexes readily homolyze, since they have such weak metal–carbon bonds. Also a kinetic "leveling effect" may come into play for the six-coordinate cobalt(II) and chromium(II) complexes because colligation occurs with ligand interchange. Such an effect would be absent for the four-coordinate molecule. Solvent exchange is itself not limiting (note $k_{ex} = 7 \times 10^9$ s^{-1} for $Cr(H_2O)_6^{2+}$);[41] rather, we suggest a competition between radical and solvent for the coordination site.

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Equilibrium. The opposing reactions of colligation and homolysis, as in eq 2, constitute a chemical equilibrium, with an equilibrium constant $K = k_{col}/k_{hom}$. Values in the $(H_2O)_2CrL^{2+}$ series are available for two R groups, as summarized in Table III.[13,14]

The similarity of the two equilibrium constants merely reflects the few compounds whose homolysis rates fall in a measurable region. Complexes with R groups such as CH_3, C_2H_5, CH_2OH and so on are much less prone to homolyze and therefore have much larger values of K. These very substantial differences in K_f are, therefore, due to the variation in k_{hom}, since the k_{col} values do not change with R. That is, variations in the strengths of the chromium–carbon bonds are contained entirely in the dissociation rates and not in those for bond formation. This is sensible, which is what makes the trend for nickel so remarkable in that rates in both directions show substantial and opposing effects.[9,10]

The rate of equilibration in eq 2 is controlled by the composite constant $k_{col}[(H_2O)_2CrL^{2+}] + k_{hom}$. Under all conditions the first term is much larger than the second and equilibrium established very rapidly, since k_{col} values are so large. Of course when a scavenger is added, the reaction, now controlled by k_{hom}, occurs slowly.

It is instructive to examine the equilibrium constants for several organometals. Values of log K are given in Table IV.

The organonickel complexes are much less stable than the organochromium complexes. This is certainly not surprising, because nickel(III) is more strongly oxidizing than chromium(III). The small values of K_f for nickel may contribute to the fact that *both* of its components, k_{col} and k_{hom}, vary with R.

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Registry No. $MV^{•+}$, 25239-55-8; $(H_2O)_2Cr([15]aneN_4)^{2+}$, 70835-04-0; $(CH_2OH)Cr([15]aneN_4)H_2O^{2+}$, 98737-23-6; $(CH(CH_3)OH)Cr([15]aneN_4)H_2O^{2+}$, 98737-26-9; $(CH_2OCH_3)Cr([15]aneN_4)H_2O^{2+}$, 137007-15-9; CH_3OH, 67-56-1; C_2H_5OH, 64-17-5; $(CH_3)_2O$, 115-10-6; CH_3, 2229-07-4; CH_2CH_3, 2025-56-1; $CH_2C_2H_5$, 2143-61-5; $CH(CH_3)_2$, 2025-55-0; $CH_2C_3H_7$, 2492-36-6; $CH(CH_3)C_2H_5$, 2348-55-2; $CH_2CH(CH_3)_2$, 4630-45-9; c-C_5H_9, 3889-74-5; $CH_2C(CH_3)_3$, 3744-21-6; CH_2OCH_3, 16520-04-0; CH_2Cl, 6806-86-6; CH_2Br, 16519-97-4; CH_2Ph, 2154-56-5.

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Kinetics and Mechanism of the Oxidation of Hexaaquavanadium(II) Ions by Alkyl Radicals

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The title reaction produces vanadium(III) ions and the corresponding hydrocarbons. The kinetics were studied by laser flash photolysis with the use of the paraquat radical ion as a kinetic probe. Results are reported for 11 radicals, consisting of primary alkyl radicals (substituted and unsubstituted) and secondary and aralkyl radicals. The rate constants are remarkably insensitive to the nature of the radical, lying in the range $(1–6) \times 10^5$ L mol^{-1} s^{-1}. The solvent kinetic isotope effects comparing $V(H_2O)_6^{2+}$ in H_2O with $V(D_2O)_6^{2+}$ in D_2O was determined for $^•CH_3$, $k_H/k_D = 3.0$. Of several mechanisms considered, we prefer one in which the radical attacks at a trigonal face of $V(H_2O)_6^{2+}$. This leads to electron transfer and a transient $(H_2O)_6VR^{2+}$ intermediates, the protonolysis of which yields the observed alkane.

Introduction

The reduction of alkyl radicals by transition-metal complexes has been reported for such reagents as $Cr(H_2O)_6^{2+}$,[1] $Co(N_4mac)^{2+}$,[2] $Ni(cyclam)^+$,[3] $Ti(H_2O)_6^{3+}$,[4] and Cu_{aq}^+.[5] It has been reported that generation of $^•CH_3$ in the presence of $V(H_2O)_6^{2+}$

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