chromatography. The $^{31}P\{^1H\}$ NMR spectrum exhibits characteristic triplet and doublet resonances at δ 87.8 and 27.7 ($^2J_{PP}$ = 102.5 Hz), and the ^1H NMR spectrum shows the expected triplet and doublet of quartets seen previously for ethyl resonances of NEt_2 groups attached to phosphorus. Mass spectra show the M^+ peak at m/e 609 and fragments at m/e 537 due to loss of NEt_2 and at m/e 217 due to the $P(S)Ph_2NEt_2^+$ ion.

Similarly, **2** and **7** are reactive toward transamination. Reaction of **2** with $P(NEt_2)_3$ in a 1:1 ratio produces **3** in a mixture with $P(NEt_2)_3$ and **1** ($P(NEt_2)_3$:**3**:**1** = 1:6:4). **7** is less reactive but also reacts with $P(NEt_2)_3$ to produce the mixed-valence compound **14**. Our results indicate that the intermediates which form in the

reaction of $P(NEt_2)_3$ with 1,2-diaminobenzene are reactive enough that they may useful in the building of longer chain P–N phosphazane molecules. Further work must be done on the condensation mixtures that are formed upon Et_2NH elimination to determine what types of products form.

Supplementary Material Available: Tables giving the details of the crystal structure determination, hydrogen atom coordinates, anisotropic thermal displacement parameters, complete bond angles and distances, and least-squares planes and dihedral angles (29 pages); listings of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

(25) Keat, R.; Sim, W.; Payne, D. S. *J. Chem. Soc. A* 1970, 2715.

Contribution from Ames Laboratory and the Department of Chemistry,
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Organochromium(III) Macrocyclic Complexes. Factors Controlling Homolytic vs Heterolytic Cleavage of the Chromium–Carbon Bond
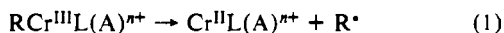
Shu Shi, James H. Espenson,* and Andreja Bakac*

Kinetics studies were done of the homolytic and heterolytic cleavage reactions of the chromium–carbon bonds in the complexes $RCr(L)A^{n+}$ (where L = [15]aneN$_4$ = 1,4,8,12-tetraazacyclopentadecane; A = H_2O, OH^-). Activation parameters (ΔH^*/kJ mol^{-1}, ΔS^*/J mol^{-1} K^{-1}) for homolysis of $RCrL(H_2O)^{2+}$ are as follows: 111 ± 2, 54 ± 6 (R = p-$CH_3C_6H_4CH_2$); 103 ± 2, 28 ± 5 ($C_6H_5CH_2$); 101 ± 3, 22 ± 9 (p-$BrC_6H_4CH_2$); 110 ± 3, 62 ± 6 (i-C_3H_7). The ΔH^* and ΔS^* parameters are considerably smaller than those for homolysis of $(H_2O)_5CrR^{2+}$ analogues. Primary alkyl macrocyclic complexes do not undergo homolysis. The complexes $RCrL(OH)^+$ slowly hydrolyze for R = n-C_3H_7 and i-C_3H_7 whereas those for which R = $ArCH_2$ do not. The activation parameters for hydrolysis are 78 ± 1, −53 ± 2 (R = i-C_3H_7) and 83 ± 3, −46 ± 9 (n-C_3H_7). This pathway shows no solvent deuterium isotope effect. The complexes $RCrL(H_2O)^{2+}$ are not subject to acidolysis by H_3O^+ or H_2O, unlike their $(H_2O)_5CrR^{2+}$ analogues.

Introduction

Conventional ligand substitution reactions of inorganic and organometallic complexes are two-electron processes. They are relatively well understood in terms of the electronic and structural factors that control the rate.[1-3] In contrast, much less is known about the factors controlling the rates of unimolecular bond homolysis reactions, L_5M^n–R → L_5M^{n-1} + R$^•$ (R = alkyl, aralkyl). The data available for complexes such as $(H_2O)_5CrR^{2+}$ [4,5] and macrocyclic organocobalt complexes[6] suggest that both steric and electronic factors must be considered.

We consider here a family of organochromium(III) macrocycles, $RCrL(H_2O)^{2+}$ (L = [15]aneN$_4$ = 1,4,8,12-tetraazacyclopentadecane) in aqueous solution. With a trans ligand A (A = H_2O, OH^-), we consider the possibilities of homolysis (eq 1) and heterolysis (eq 2). Neither reaction type has been examined previously for these complexes.

$$RCr^{III}L(A)^{n+} \rightarrow Cr^{II}L(A)^{n+} + R^• \qquad (1)$$

$$RCr^{III}L(A)^{n+} + H_2O \rightarrow HOCr^{III}L(A)^{n+} + RH \qquad (2)$$

The presence of the macrocyclic ligand offers certain advantages in studying the reactivity of the metal–carbon bond. Most sig-

nificantly, the macrocycle permits variation of the pH over a wide range, in contrast to the complexes $(H_2O)_5CrR^{2+}$ that rapidly decompose above pH ∼ 4. This allows examination of the species with A = OH^-. In this article we present data showing that variation of A changes the mechanism of the Cr–C bond cleavage from homolytic to heterolytic. We explain this finding by the stabilizing effect of the strongly electron-donating OH^- group on the 3+ oxidation state of chromium. The same phenomenon helps in the understanding of the reactivity order when the R group is changed.

Experimental Section

Materials. The complexes $RCrL(H_2O)^{2+}$ were prepared by the known reaction of RBr or RI with $(H_2O)_2CrL^{2+}$ and separated by ion-exchange chromatography on Sephadex C25 columns.[7] The electronic spectra matched the reported values.[7] Radical scavengers were [Co(NH$_3$)$_5$-Br](ClO$_4$)$_2$[8] and HTMPO^9 (Aldrich). The ESR and UV–visible spectra of HTMPO matched the literature values.[10]

Techniques. ESR spectra were recorded on aqueous solutions with an IBM-Bruker ER-200 spectrometer. Since the activation energies of metal–alkyl homolysis are in general rather large,[4-6] homolysis can be promoted at elevated temperature. This approach was used to conduct the ESR study. Samples of the complex $RCrL(A)^{n+}$ in the presence of a 3-fold excess of HTMPO were immersed in a water bath at 40 °C to initiate decomposition. At a fixed time, decomposition was quenched by immersing the sample in an ice–water bath. The sample was then warmed back to 15 °C and the ESR spectrum recorded. With bath temperature and timing controlled, the method was reproducible.

(1) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978; p 190.
(2) Green, M. In *Mechanisms of Inorganic and Organometallic Reactions*; Twigg, M. V., Ed.; Plenum Press: New York, 1983; Vol. 1, p 221.
(3) Johnson, M. D.; Winterton, N. *J. Chem. Soc. A* 1970, 511.
(4) (a) Espenson, J. H. *Adv. Inorg. Bioinorg. Mech.* 1982, *1*, 1. (b) *Prog. Inorg. Chem.* 1983, *30*, 189.
(5) Nohr, R. S.; Espenson, J. H. *J. Am. Chem. Soc.* 1975, *97*, 3392.
(6) Halpern, J. *Acc. Chem. Res.* 1982, *15*, 238.

(7) Samuels, G. J.; Espenson, J. H. *Inorg. Chem.* 1979, *18*, 2587.
(8) Diehl, H.; Clark, H.; Willard, H. H. *Inorg. Synth.* 1939, *1*, 186.
(9) HTMPO = 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxyl.
(10) Mossoba, M. M.; Makino, K.; Riesz, P. *J. Phys. Chem.* 1984, *88*, 4717.

A)

B)
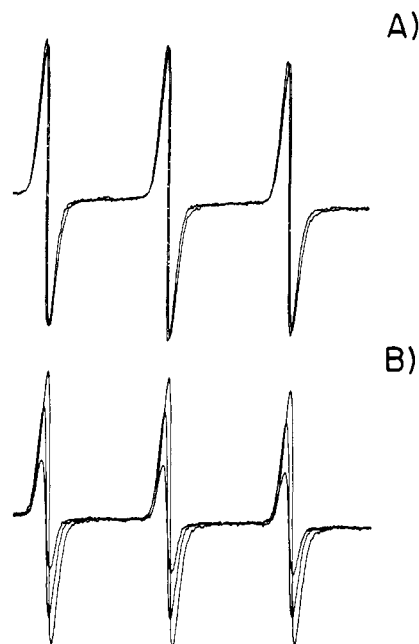
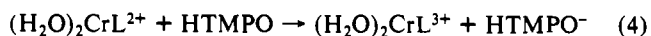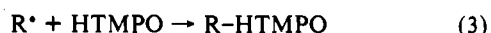**Figure 1.** Changes in the ESR spectrum of the radical scavanger HTMPO in the presence of i-C$_3$H$_7$CrL(H$_2$O)$^{2+}$ (B) and i-C$_3$H$_7$CrL-(OH)$^+$ (A) (L = [15]aneN$_4$). The spectra of reaction solutions that were kept at 40 °C for 0 and 15 min (A) and 0, 2, and 12 min (B) were recorded at 15 °C, with a sweep width of 50 G. Small fluctuations of frequency with time causes small shifts of the central field around 3475 G.

Organic products were identified with a Hewlett-Packard Model 5790 gas chromatograph, with a 6 ft × $^1/_8$ in. column packed with OV-101 or VZ-10 stationary phases. The gas chromatograph was calibrated with standard organic halides and hydrocarbons. Electronic spectra were recorded with a Perkin-Elmer Lambda Array 3840 diode array spectrophotometer.

Kinetic Measurements. The homolytic decomposition of the organo-chromium macrocycles RCrL(H$_2$O)$^{2+}$ was monitored spectrophotomet-rically at their absorption maxima: λ 287 and 400 nm for R = i-C$_3$H$_7$, 359 nm for p-CH$_3$C$_6$H$_4$CH$_2$, 353 nm for C$_6$H$_5$CH$_2$, and 360 nm for p-BrC$_6$H$_4$CH$_2$. These measurements were carried out under an argon atmosphere on solutions containing 0.010 M HClO$_4$ and 0.20 M NaClO$_4$. The heterolytic decomposition in basic solutions was monitored at 274 nm (R = i-C$_3$H$_7$) and 260 nm (n-C$_3$H$_7$) at [OH$^-$] = 7.2–160 mM, μ = 0.20 M. Some experiments, including the temperature dependence, were done at [OH$^-$] = μ = 0.82 M. In every case temperature was precisely controlled by immersing the quartz cuvette in a water bath positioned in the light beam of the spectrophotometer; thermostated water was circulated through the jacket of the water bath. Organochromium macrocycles were used as limiting reagents in both homolysis and het-erolysis studies. The kinetic data were obtained by means of a Cary Model 14 spectrophotometer that had been converted to a computer-controlled instrument by On Line Instrument Systems. The OLIS data station also provided the least-squares program for the analysis of the absorbance–time data according to the first-order equation $A_t = A_\infty + (A_0 - A_\infty)e^{-kt}$.

Results

Bond Homolysis. Unimolecular homolysis of the chromium–carbon bond was observed for secondary alkyl and aralkyl chromium complexes RCrL(H$_2$O)$^{2+}$ in slightly acidic ([H$^+$] = 1.0 × 10^{-2} M) solutions in the presence of free-radical scavengers. For example, some experiments were conducted in the presence of the persistent free radical HTMPO,[9] which is known[11] to capture in situ generated free radicals (eq 3). We found that HTMPO also reacts rapidly with (H$_2$O)$_2$CrL^{2+} (eq 4). The ESR technique

$$R^\bullet + HTMPO \rightarrow R\text{-}HTMPO \tag{3}$$

$$(H_2O)_2CrL^{2+} + HTMPO \rightarrow (H_2O)_2CrL^{3+} + HTMPO^- \tag{4}$$

was employed in this study to estimate the rate of homolysis. The

(11) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 5197.

Table I. Rate Constants for the Homolysis of RCr([15]aneN$_4$)(H$_2$O)$^{2+}$ Complexes in Aqueous Solutions[a]

R	scavenger, concn/mM	$10^4 k_6/s^{-1}$
i-C$_3$H$_7$	(NH$_3$)$_5$CoBr^{2+}, 0.63–4.65	5.0 ± 0.3
i-C$_3$H$_7$	HTMPO, 0.20–1.60	5.0 ± 0.4
p-CH$_3$C$_6$H$_4$CH$_2$	HTMPO, 0.31–1.67	1.36 ± 0.01
C$_6$H$_5$CH$_2$	HTMPO, 0.76–2.00	1.24 ± 0.04
p-BrC$_6$H$_4$CH$_2$	HTMPO, 0.23–1.00	1.15 ± 0.01

[a]At 25.0 °C with [H$^+$] = 1.0 × 10^{-2} M at μ = 0.20 M and with [RCr([15]aneN$_4$)(H$_2$O)$^{2+}$]$_0$ = 0.02–0.35 mM, used always as a limit-ing reagent.
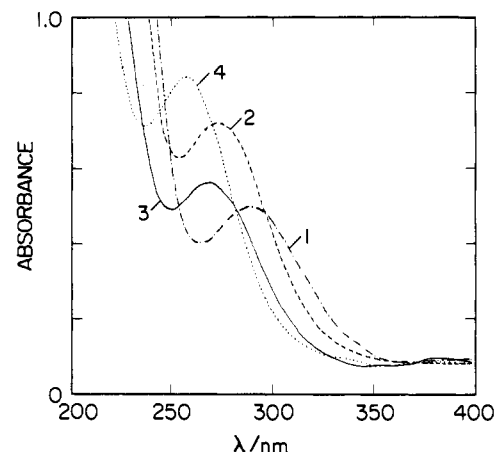
Figure 2. Electronic spectra of RCrL(A)$^{n+1}$ complexes (L = [15]aneN$_4$; optical path length = 1 mm): (1) 1.5 mM i-C$_3$H$_7$CrL(H$_2$O)$^{2+}$ at pH 4; (2) 1.5 mM i-C$_3$H$_7$CrL(OH)$^+$ at pH 7; (3) 2.2 mM n-C$_3$H$_7$CrL(H$_2$O)$^{2+}$ at pH 4; (4) 2.2 mM n-C$_3$H$_7$CrL(OH)$^+$ at pH 7.

intensity of the ESR signal of HTMPO decreased as the homolysis of the isopropylchromium complex proceeded (Figure 1).

Another scavenger is (NH$_3$)$_5$CoBr^{2+}, which reacts with free radicals[12] (eq 5) and with the chromium(II) macrocycle[13] (eq 6). Because of their dual functions both HTMPO and (NH$_3$)$_5$CoBr^{2+} are effective scavengers in this system.

$$(NH_3)_5CoBr^{2+} + R^\bullet \xrightarrow{H_3O^+} RBr + Co_{aq}^{2+} + 5NH_4^+ \tag{5}$$

$$(NH_3)_5CoBr^{2+} + (H_2O)_2CrL^{2+} \xrightarrow{H_3O^+} \\ BrCrL(H_2O)^{2+} + Co_{aq}^{2+} + 5NH_4^+ \tag{6}$$
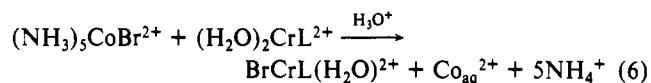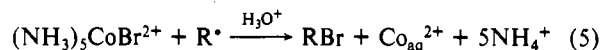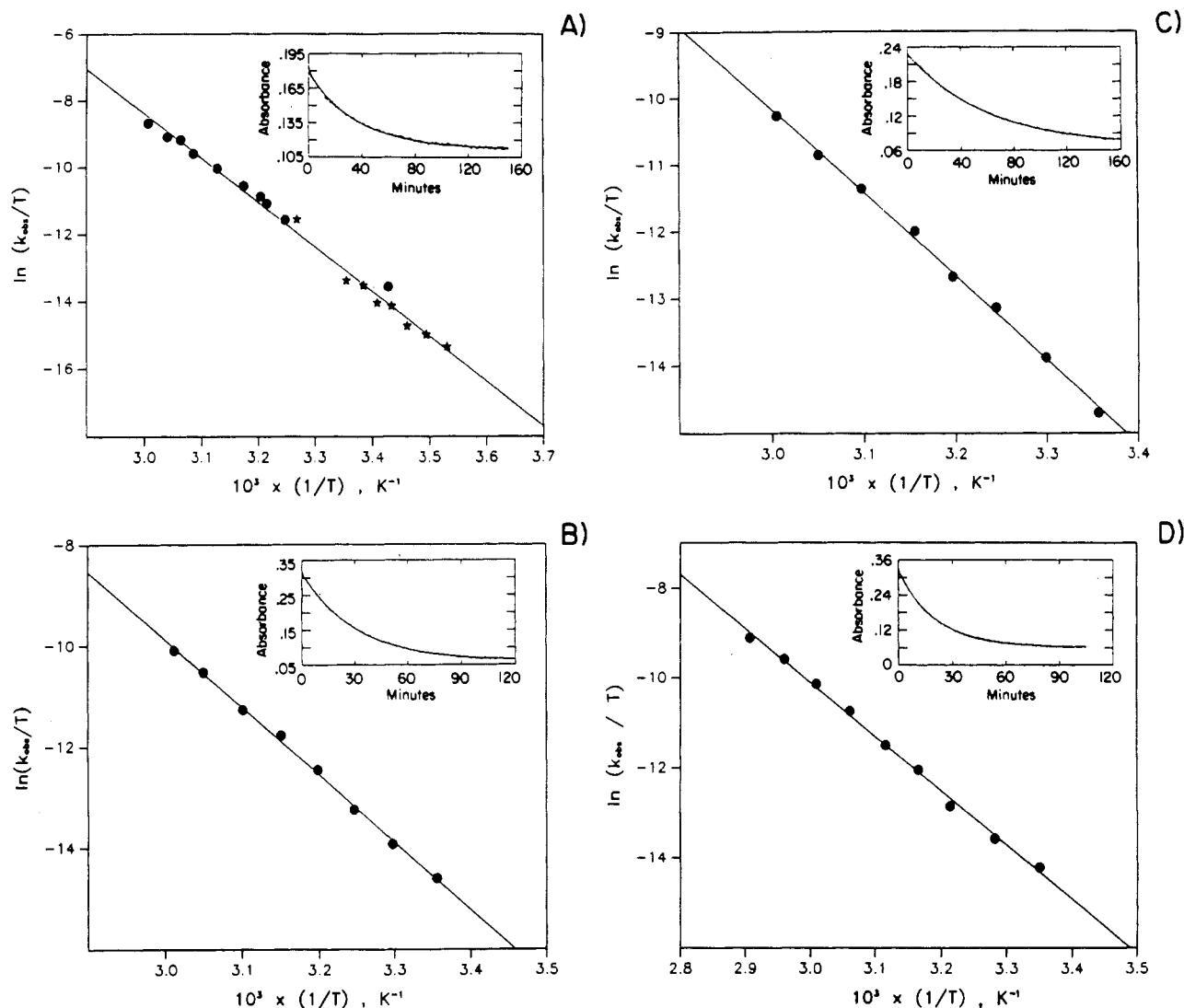
The analysis of organic products by GC confirmed that hom-olysis is the only reactivity mode in acidic solutions for all the complexes examined. For example, the reaction of i-C$_3$H$_7$Cr-([15]aneN$_4$)$^{2+}$ in the presence of (NH$_3$)$_5$CoBr^{2+} yielded i-C$_3$H$_7$Br as the exclusive organic product, consistent with the sequence of reactions 1 and 5.[12] No propane was detected, which effectively rules out any heterolysis under these conditions.

Quantitative kinetic studies of the homolysis were conducted spectrophotometrically in the presence of either HTMPO or (NH$_3$)$_5$CoBr^{2+}. The reactions (eq 7) are first order with respect to the concentration of the organochromium macrocycle and zero order with respect to the scavenger concentration (eq 8). The concentration conditions and rate constants are summarized in Table I.

$$RCrL(H_2O)^{2+} \xrightarrow{H_2O} R^\bullet + CrL(H_2O)_2^{2+} \tag{7}$$

$$-d[RCrL(H_2O)^{2+}]/dt = k_7[RCrL(H_2O)^{2+}] \tag{8}$$
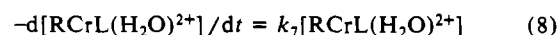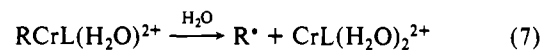
No homolytic cleavage of the Cr–C bond was observed for RCrL(H$_2$O)$^{2+}$ when R was a primary alkyl group, as tested for

(12) Kelley, D. G.; Bakac, A.; Espenson, J. H. *Inorg. Chem.*, in press.
(13) Qualitative tests showed a very rapid reaction between (H$_2$O)$_2$CrL^{2+} and (NH$_3$)$_5$CoBr^{2+}. The cobalt(III) complex is also reduced very rapidly by Cr(H$_2$O)$_6$$^{2+}$ (Candlin, J. P.; Halpern, J.; Trimm, D. L. *J. Am. Chem. Soc.* **1964**, *86*, 1019).

Figure 3. Temperature dependence according to the activated complex theory of homolysis rate of (A) i-$C_3H_7CrL(H_2O)^{2+}$, (B) p-$CH_3C_6H_4CH_2CrL(H_2O)^{2+}$, (C) $C_6H_5CH_2CrL(H_2O)^{2+}$, and (D) p-$BrC_6H_4CH_2CrL(H_2O)^{2+}$ (L = [15]aneN$_4$). Insets show observed kinetic profiles along with fitted pseudo-first-order curves: (A) 298.0 K; (B) 317.4 K; (C) 303.7 K; (D) 311.1 K. In (A), data were taken with $(NH_3)_5CoBr^{2+}$ (stars) and with HTMPO (circles) as radical scavengers.

$R = C_2H_5$, n-C_3H_7, and n-C_4H_9. Indeed, in the absence of a scavenger even the secondary alkyl and aralkyl complexes do not undergo net homolysis because the reverse of reaction 7 occurs rapidly. Thus these organochromium macrocycles can be stored for weeks when kept in a refrigerator under nitrogen or argon.

Trans Effect on Homolysis of the Hydroxo Complexes. A change of pH from 4 to 6 of a solution of $RCrL(H_2O)^{2+}$ causes an instantaneous color change from yellow to red. The associated spectral changes are shown in Figure 2. When the solution is reacidified, the yellow color is restored and the spectrum of $RCrL(H_2O)^{2+}$ reappears. The reversibility of the spectral changes indicates that the chromium–carbon bond remains intact; reversible deprotonation of the trans water molecule yields $RCrL(OH)^{+}$.[14,15]

The progress of the homolysis was monitored by the ESR signal of the scavenger HTMPO. As shown in Figure 1A, the intensity of the ESR spectrum of HTMPO in the presence of i-$C_3H_7CrL(OH)^+$ remains virtually unchanged after 15 min at 40 °C. In contrast, the decreasing ESR signal (Figure 1B) shows a significant loss of HTMPO during the homolysis of i-$C_3H_7CrL(H_2O)^{2+}$ in ~12 min at 40 °C. This establishes that the homolysis rate of the hydroxo complex is negligibly small

compared to that of the aqua complex.

Temperature Dependence of Homolysis Rate Constants. The value of k_7 was determined over a range of temperatures for each of the complexes $RCrL(H_2O)^{2+}$ with either $(NH_3)_5CoBr^{2+}$ or HTMPO used to draw the reaction to completion. The R group and the temperature range for each are as follows: i-C_3H_7, 286–333 K; p-$CH_3C_6H_4CH_2$, 295–332 K; $C_6H_5CH_2$, 298–333 K; p-$BrC_6H_4CH_2$, 298–344 K (as shown in Figure 3). The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were determined from a fit of the data to the Eyring equation, to which they nicely conformed. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are summarized in Table II.

Heterolytic Cleavage of the Cr–C Bond. Although the trans aqua organochromium macrocyclic cations do not undergo aci-

Table II. Activation Parameters for the Homolysis and Heterolysis of Organochromium Cations[a]

complex	reaction	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}
i-$C_3H_7CrL(H_2O)^{2+ b}$	homolysis	110 ± 3	62 ± 6
p-$CH_3C_6H_4CH_2CrL(H_2O)^{2+ b}$	homolysis	111 ± 2	54 ± 6
$C_6H_5CH_2CrL(H_2O)^{2+ b}$	homolysis	103 ± 2	28 ± 5
p-$BrC_6H_4CH_2CrL(H_2O)^{2+ b}$	homolysis	101 ± 3	22 ± 9
$(H_2O)_5CrCH_2C_6H_5^{2+ c}$	homolysis	133	153
i-$C_3H_7CrL(OH)^{+ d}$	heterolysis	78 ± 1	-53 ± 2
n-$C_3H_7CrL(OH)^{+ d}$	heterolysis	83 ± 3	-42 ± 9

^{a} L = [15]aneN$_4$. ^{b} In aqueous solution with 1.0 × 10^{-2} M H$^+$ at μ = 0.20 M. ^{c} Reference 5. ^{d} [NaOH] = μ = 0.82 M.

(14) The protonation and deprotonation of a nitrogen of L can probably be ruled out at this pH. Also, the deprotonation of a coordinated molecule of H$_2$O in $(H_2O)_2CrL^{3+}$ is known to have a pK_a of 2.9.[15]

(15) Richens, D. T.; Adzamli, I. K.; Leupin, P.; Sykes, A. G. *Inorg. Chem.* **1984**, *23*, 3065.

dolysis in acidic solutions (at least not in comparison with the dominant homolysis reaction), the situation is different for the hydroxo complexes RCrL(OH)$^+$ at pH 12–14. Here, the complexes with R = i-C$_3$H$_7$ and n-C$_3$H$_7$ both undergo slow hydrolysis (eq 9) to yield propane as the only organic product detected gas

$$RCrL(OH)^+ + H_2O \rightarrow RH + CrL(OH)_2^+ \qquad (9)$$

chromatographically. Both the kinetics and the organic products are unaffected by the presence of HTMPO and (NH$_3$)$_5$CoBr^{2+}. This clearly rules out any contribution from a homolytic pathway. The nature of the chromium product in eq 9 was assumed but not verified. No decomposition of the aralkylchromium complexes was observed in basic solutions.

The rate of reaction 9 follows first-order kinetics, with k_9 = (2.3 ± 0.2) × 10^{-4} s^{-1} for R = i-C$_3$H$_7$ and (6.6 ± 0.3) × 10^{-5} s^{-1} for R = n-C$_3$H$_7$ at 25 °C. The values of k_9 are independent of [OH$^-$] in the range 7.2–160 mM at μ = 0.20 M and in the range 0.16–1.0 M at nonconstant ionic strength. The variation of temperature (298–338 K) gave the activation parameters ΔH^* = 78 ± 1 kJ mol^{-1}, ΔS^* = –53 ± 2 J mol^{-1} K^{-1} for R = i-C$_3$H$_7$ and ΔH^* = 83 ± 3 kJ mol^{-1}, ΔS^* = –46 ± 9 J mol^{-1} K^{-1} for R = n-C$_3$H$_7$, as shown in Table II. The rate constant for n-C$_3$H$_7$CrL(OD)$^+$ in D$_2$O was also measured, with k_9 = 6.2 × 10^{-5} s^{-1} at 25.0 °C.

Discussion

The instantaneous and reversible optical change (Figure 2) in the pH range 4–6 has been assigned to the conversion of RCrL-(H$_2$O)$^{2+}$ to RCrL(OH)$^+$. The lowest energy charge-transfer (R → Cr) band shifts to higher energy in basic solution, consistent with the π-donor ability of OH$^-$, which increases the energy of the "t$_{2g}$" orbitals, resulting in a higher energy for the R → Cr charge-transfer transition. Put differently, RCrL(OH)$^+$ is a weaker oxidant than RCrL(H$_2$O)$^{2+}$.

The existence of both aqua and hydroxo complexes allows the study of the homolysis of both species. For the secondary alkyl and aralkyl aqua complexes, the reaction is indeed homolysis based on the following evidence: (a) the reaction proceeds in the presence of scavengers for both R$^\bullet$ and (H$_2$O)$_2$CrL^{2+}; (b) the rate constant remains independent of the scavenger concentration; (c) the rate constant is independent of which scavenger was used but varies with the group R. The primary alkyl complexes do not undergo homolysis even over very long times. This is consistent with the lower thermodynamic stability of primary alkyl radicals as compared to secondary and aralkyl radicals.

Under the same concentration and temperature conditions, none of the hydroxo complexes, RCrL(OH)$^+$, undergoes homolysis. This is again related to the electron-donating effect of OH$^-$, which stabilizes the Cr(III) state and thus makes it less susceptible to internal electron transfer that accompanies homolysis of eq 7.

The activation parameters for bond homolysis are listed in Table II. The large values of ΔH^* reflect the large chromium–carbon bond strengths of these complexes. Indeed, they can be taken as an approximate measure of the bond dissociation enthalpy, once allowance is made for the relatively small value of ΔH^*_{-7} for the radical recombination reaction.[6,16] The value of ΔH^* for (H$_2$O)$_5$CrCH$_2$Ph^{2+} (133 kJ mol^{-1}) is significantly larger than the value of 103 kJ mol^{-1} for its macrocyclic analogue. This difference in ΔH^* can be explained on the basis of the molecular structures, in particular the longer Cr–C bond in the macrocycle.[17] The compound [p-BrC$_6$H$_4$CH$_2$CrL(H$_2$O)](ClO$_4$)$_2$·THF has a Cr–C bond length of 2.14 Å,[17] noticeably longer than the 2.06 Å distance in *trans*-[CH$_2$ClCr(acac)$_2$H$_2$O].[18] No complex in the [(H$_2$O)$_5$CrR]X$_2$ series has been crystallized, although one anticipates a Cr–C bond as short as or shorter than that in the acac derivative. This argument is, however, somewhat speculative, since the overall charge is different in the pentaaqua and acac series.

The observed effect of the macrocycle on the Cr–C bond strength is the net result of two opposing effects, steric and electronic. The former weakens and lengthens the bond. The electron donation from the N$_4$ macrocycle, on the other hand, stabilizes the Cr(III) state and thus inhibits homolysis. The size of the electronic effect of [15]aneN$_4$ becomes obvious if one compares the reduction potentials for the couples Cr([15]-aneN$_4$)(H$_2$O)$_2$$^{3+/2+}$ (–0.58 V)[7] and Cr(H$_2$O)$_6$$^{3+/2+}$ (–0.41 V). Yet, despite the electronic effect favoring the Cr(III) state, the Cr–C bond is weaker in the macrocyclic series. This point illustrates just how dominant steric effects are on bond strengths, a point made already in earlier work.[19,20]

Despite the lowering of ΔH^* for the macrocycle, the homolysis of (H$_2$O)$_5$CrCH$_2$Ph^{2+} (k = 2.6 × 10^{-3} s^{-1})[5] proceeds more rapidly than that of the analogous PhCH$_2$CrL(H$_2$O)$^{2+}$ (1.2 × 10^{-4} s^{-1}). This, of course, is due to the more-than-offsetting values of ΔS^*. The complex (H$_2$O)$_5$CrCH$_2$Ph^{2+} has a ΔS^* value of 153 J mol^{-1} K^{-1}, as compared to 28 J mol^{-1} K^{-1} for (H$_2$O)Cr(L)CH$_2$Ph^{2+}. This large difference seems to indicate that the second coordination sphere "loosens up" much more in reaching the transition state in the aqua series. This is not unreasonable given that (H$_2$O)$_5$CrR^{2+} must be much more strongly solvated than the macrocyclic analogues and that in reaching the transition state for homolysis the bond distances approach those for Cr(II) complexes. This means that the Cr–O distances in [(H$_2$O)$_5$Cr---R^{2+}]* stretch significantly, whereas the Cr–N bond lengths in [([15]-aneN$_4$)(H$_2$O)Cr---R^{2+}]* remain virtually the same. Thus the effect on the second coordination sphere must be quite dramatic for (H$_2$O)$_5$CrR^{2+} but negligible in the macrocyclic series. In addition, there is a contribution from the rotational entropy changes of the coordinated molecules of water in (H$_2$O)$_5$CrR^{2+}, a gain that has no counterpart in the macrocyclic series.

The rate constants for homolysis of ArCH$_2$CrL(H$_2$O)$^{2+}$ vary little as the substituent on the benzene ring changes from p-CH$_3$ to H to p-Br. This is different from the behavior of the corresponding pentaaqua series, p-X-C$_6$H$_4$CH$_2$Cr(H$_2$O)$_5$$^{2+}$, where the Hammett correlation yields the reaction constant ρ = –1.01.[5] The greater sensitivity to substituents in the pentaaqua complexes is qualitatively consistent with the Cr–C bond being stronger for them. A greater degree of charge transfer in the transition state is required for homolysis of (H$_2$O)$_5$CrCH$_2$Ar^{2+} as compared to ArCH$_2$Cr(L)H$_2$O^{2+}.

Turning to the pathway for the heterolytic solvolysis reation, we note that RCrL(OH)$^+$ is not attacked by external OH$^-$; i.e., the rate is independent of [OH$^-$]. This compares with the behavior of (H$_2$O)$_5$CrR^{2+} complexes, where inverse [H$^+$] terms signal a conjugate base pathway that is significant enough to provide the major decomposition route at pH 4–7.[21,22] With the macrocycles we find that only the hydroxo complexes, but not the aqua, are subject to heterolytic decomposition. It is significant and interesting that a reaction of the aqua complex with H$_3$O$^+$ is not important. Even though H$_3$O$^+$ itself might function as an electrophile, there is no kinetically significant term with a direct dependence on [H$_3$O$^+$], unlike the pentaaqua series where a term k_A[(H$_2$O)$_5$CrR^{2+}][H$_3$O$^+$] provides, for most R groups, a major pathway.[4] This means that proton transfer to an incipient carbanion is not important for chromium–carbon bond heterolysis of RCrL(OH)$^+$ complexes.

How is the rate law, which has the form k_9[RCrL(OH)$^+$], to be interpreted? One can hardly attribute it to a path in which the external H$_2$O molecule acts as a kinetically active electrophile, given the inactivity of the more powerful electrophile H$_3$O$^+$ toward the aqua complex. Moreover, we find no kinetic isotope effect in D$_2$O: the complex n-C$_3$H$_7$CrL(OD)$^+$ has k_9 = 6.2 × 10^{-5} s^{-1} (25 °C, pD = 12 in D$_2$O), compared to k_9 = (6.6 ± 0.3) × 10^{-5} s^{-1} for the reaction of n-C$_3$H$_7$CrL(OH)$^+$ in H$_2$O. Thus proton

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transfer from H_2O to R is not significantly advanced in the transition state.

The heterolytic reactions are accompanied by substantial and negative activation entropies, as shown in Table II. This suggests a transition state with larger charge separation as compared to that of reactant. Hence, the interpretation we offer is that the rate-limiting step is intramolecular charge transfer to form an incipient carbanion, and the transition state might be represented as $[HOCr^{\delta+}(L)R^{\delta-}\cdots H-OH^+]^{\ddagger}$. We further note that heterolysis applies only to the complex in which the trans ligand is OH^-, not H_2O. The evident role for coordinated OH^- is to act as a strong electron donor, which improves the energetics of carbanion for-

mation.

The aralkyl complexes are not subject to heterolytic solvolysis, even in the case of the trans hydroxy species. This contrasts with the very slow but easily observed decomposition of $(H_2O)_5CrCH_2Ph^{2+}$.[23]

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Solvent-Dependent Redox Thermodynamics of Metal Amine Complexes. Delineation of Specific Solvation Effects

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Solvent-dependent formal potentials, E_f, and reaction entropies, $\Delta S_{rc}°$, for four reversible Co(III/II) couples featuring macrobicyclic "cage" ligands have been obtained. These are utilized, together with corresponding data for other Co(III/II) and Ru(III/II) amine couples and for M(III/II) polypyridine couples, to unravel effects on the redox thermodynamics arising from specific ligand–solvent and other interactions. The solvent dependencies of E_f (vs ferrocenium–ferrocene) for each redox couple are fitted by using a multiparameter approach, incorporating various well-known empirical quantities describing solvent basicity, acidity, polarity, and internal ordering. For most amine couples, solvent basicity appears to play a prevailing role, associated with interactions involving the amine hydrogens, although solvent polarity also exerts a substantial, albeit less solvent-dependent, influence upon E_f. The presence of a deprotonated amide group in the Co(III/II) amine couple is signaled by the additional presence of a significant solvent acidity component in the multiparametric fit. The solvent basicity and other specific contributions to the E_f–solvent behavior for the polypyridine couples are markedly smaller than for the amines. While the inclusion of a "solvent internal ordering" term does not exert a statistically significant influence on the E_f–solvent dependence for any of the redox couples, the $\Delta S_{rc}°$–solvent dependencies are correlated most successfully with this parameter. Besides identifying the major specific solvation factors upon the redox thermodynamics for such inorganic redox couples, the present multiparametric solvent-dependent analysis also provides a novel, although approximate, means by which the extent of such obfuscating influences upon E_f can be assessed.

Introduction

The ways in which outer-sphere effects such as solvation and the nature of the counterion affect the kinetics and the thermodynamics of electron transfer are incompletely understood. In order to explore these issues, an examination of the solvent-dependent formal potentials, E_f, of redox couples provided by cobalt "cage" complexes[1–7] is likely to be useful. A key feature of the macrobicyclic ligands of such complexes is that they render the normally labile high-spin Co(II) oxidation state substitutionally inert.[3,7–9] These redox couples are therefore free of complications due to ligand loss in the Co(II) oxidation state and exhibit chemical and electrochemical reversibility.[3,7–13] Limited data are also available on the redox properties of cage complexes in nonaqueous solvents.[7,8,11] One aim of the work described here is to expand on these results.

In addition to the cage complexes, the solvent dependencies of the $[Ru(NH_3)_6]^{3+/2+}$ and $[Co(en)_3]^{3+/2+}$ formal potentials (en = 1,2-ethanediamine) have been reexamined in the present study; previous investigations have shown that E_f values for these couples correlate with solvent basicity.[11,14,15] A complication with the latter redox couple is that $[Co(en)_3]^{2+}$ is labile, so that it is often necessary to add 1,2-ethanediamine in order to prevent irreversible reduction.[11] By analogy with the significant observed effect of added 1,2-ethanediamine on E_f for the $[Ru(en)_3]^{3+/2+}$ couple,[13] the addition of 1,2-ethanediamine to the solvents of interest is likely

to influence the thermodynamic parameters obtained from the solvent dependence of the $[Co(en)_3]^{3+/2+}$ couple. The cage complexes can therefore provide a less ambiguous indicator of the

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