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Kinetics of the Reduction of Alkyl Halides by a Chromium(II) Macrocycle

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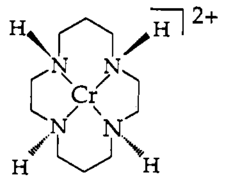
The [14]aneN$_4$ ligand[1] and its relatives readily form complexes with cobalt(II),[2,3] nickel(II),[4–8] and other metals.[9] The chromium complexes of the ligand [14]aneN$_4$ have also been known for a number of years,[10–13] but it has not been until recently that the synthetic procedures have been developed to yield the *trans*-dichloro and *trans*-diaqua isomers in good purity and yield.[14]



trans-Cr([14]aneN$_4$)$^{2+}$ (LCr^{2+})

With the availability of pure samples of *trans*-[$(H_2O)_2CrL$](CF_3SO_3)$_3$,[14] where [14]aneN$_4$ is now abbreviated as L, it is feasible to undertake studies of the complex *trans*-[$(H_2O)_2CrL$]$^{2+}$. The moderately long lifetime of *trans*-[$(H_2O)_2CrL$]$^{2+}$ in air-free *acidic* solutions (several hours at pH 2–3 at 0 °C) gives this complex a great advantage over the related $(H_2O)_2$Cr([15]aneN$_4$)$^{2+}$, which demetalates readily upon acidification.

The reduction of alkyl halides is a subject that has been of mechanistic interest for over two decades. Much effort has been expended in distinguishing among electron-transfer, atom-transfer, and oxidative-addition mechanisms.[16] With the new $(H_2O)_2CrL^{2+}$ species available, we have returned to a reaction type that we[15,17,18] and others[19–23] have considered before. Here we are reporting data on the stoichiometry, kinetics, and products of the reduction of alkyl halides according to the equation

$$RX + 2(H_2O)_2CrL^{2+} = (H_2O)LCr{-}R^{2+} + (H_2O)LCr{-}X^{2+} + 2H_2O \quad (1)$$

Experimental Section

Materials. Perchloric and hydrochloric acids, both Merck, were used without further purification. Trifluoromethanesulfonic acid (3M, FC-24) was distilled before use. Lithium perchlorate, prepared by neutralizing lithium carbonate (Merck) with perchloric acid, was recrystallized three times from water. Alkyl halides (Aldrich and Fluka) were distilled as needed. *tert*-Butyl alcohol (Kemika) was distilled before use. Doubly distilled water, additionally purified through a Milli-Q system, was used throughout.

Solutions of $(H_2O)_2CrL^{2+}$ were prepared by zinc-amalgam reduction of the corresponding chromium(III) complex. The starting [$(H_2O)_2CrL$](CF_3SO_3)$_3$ was prepared as recently described.[14]

Techniques and Procedures. All the experiments were performed under an atmosphere of argon, which was passed over a copper catalyst and scrubbed through a Cr^{2+} solution. The products were separated on a column of Sephadex C-25 ion-exchange resin which was kept at 0 °C to slow down the decomposition of the organochromium(III) complexes. The chromium content of the ion-exchanged solutions was determined by a standard procedure[25] after the macrocycle was destroyed by gentle heating of a small sample with an equal volume of concentrated $HClO_4$. *Warning! Although we experienced no difficulties with this procedure, precautions are necessary. A boiling mixture of perchloric acid and organic matter is potentially explosive.*

The redox potential for the [$(H_2O)_2CrL$]$^{3+/2+}$ couple was determined by cyclic voltammetry using a PAR 704 apparatus.

A Cary 219 spectrophotometer was used for spectral identifications and titrations and for the kinetic runs with $t_{1/2} > 10$ s. For faster kinetics, a Durrum D-110 stopped-flow instrument was used. The kinetics were followed at the absorption maxima of the organochromium(III) products (350–382 nm, Table I). The data were collected under pseudo-first-order conditions by use of a large excess of organic halides over $(H_2O)_2CrL^{2+}$. Most of the reactions used water as solvent, although in several instances a 1:1 mixture of *tert*-butyl alcohol/water was used. This made it possible to compare directly the data to those for the closely related $(H_2O)_2$Cr([15]aneN$_4$)$^{2+}$, which was studied previously in the mixed solvent.

Results

The reduction potential for the couple $(H_2O)_2CrL^{3+/2+}$ was determined in 0.4 M aqueous $HClO_4$. At this acidity, virtually all the Cr(III) complex is present in the diaqua form (pK^1_a = 3.05 at μ = 0.1 M).[11] The value obtained, $E_{1/2} = -0.86$ V vs Ag/AgCl electrode (−0.64 V vs NHE), is consistent with the reported values and trends in the less acidic solutions.[26]

The stoichiometry of several reactions was determined by spectrophotometric titrations at wavelengths of maximum absorption of the organochromium complexes formed, as shown for CH_3I in Figure 1. The values of the ratio [RX]/[$(H_2O)_2CrL^{2+}$] in aqueous solutions (0.01 M $HClO_4$) were 0.48 (CH_3I), 0.50 (C_2H_5Br), and 0.40 ($PhCH_2Cl$). The titration with C_2H_5Br was also carried out in 1:1 *tert*-butyl alcohol/H_2O and yielded a ratio of 0.46. After the completion of the titrations, the yields of the organochromium ions, $(H_2O)LCrR^{2+}$, were determined from the UV–visible spectra. Typically, the values were 35–50% of the total chromium. All the results confirm the overall 1:2 stoichiometry of eq 1. The extreme oxygen sensitivity of $(H_2O)_2CrL^{2+}$ is believed responsible for the small deviations from the ideal ratio of 0.50.

Several organochromium complexes were prepared on a larger scale, ion-exchanged, and characterized by their UV–visible spectra (Table I).

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[1] We abbreviate 1,4,8,11-tetraazacyclotetradecane as [14]aneN$_4$ or cyclam.

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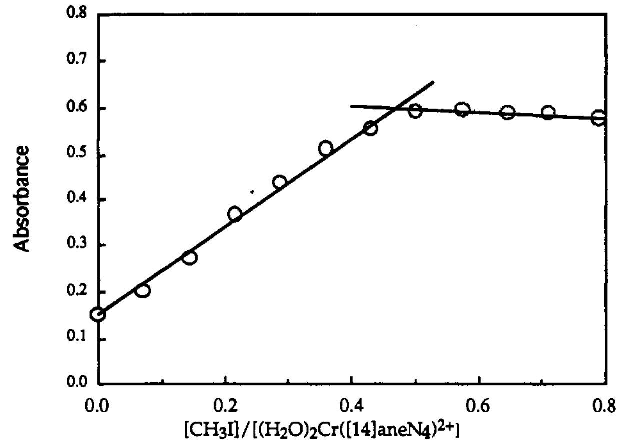

Figure 1. Spectrophotometric titrations of 2.5 mM *trans*-Cr([14]aneN$_4$)(H$_2$O)$_2^{2+}$ with methyl iodide at λ 360 nm.

Table I. Spectral Data for *trans*-(H$_2$O)([14]aneN$_4$)CrR^{2+} Complexes

R	λ_{max}/nm (ϵ/M^{-1} cm^{-1})		
H_2O^a	350 (48.8)	404 (34)	540 (18.9)
CH_3	245 (2475)	360 (238)	435 (63)
C_2H_5	260 (2320)	370 (289)	435 (69.2)
1-C_3H_7	265 (2810)	372 (304)	430 (68.6 sh)
1-C_4H_9	265 (2300)	372 (304)	430 (63.5 sh)
2-C_3H_7	265 (1900), 274 (1910), 285 (1910)	382 (270)	
$C_6H_5CH_2$	274 (1930)	290 (1630)	350 (430)

[a] Charge 3+.

Table II. Kinetic Data for the Reactions of Organic Halides with *trans*-(H$_2$O)$_2$Cr([14]aneN$_4$)$^{2+}$

	k_{RX}/M^{-1} s^{-1} ^{a}	
RX	H_2O	1:1 *t*-BuOH/H_2O
CH_3I	0.325	0.0850
C_2H_5Br	1.48	0.430
1-C_3H_7Br	1.33	0.350
1-C_4H_9Br	1.50	0.445
2-C_3H_7Br	16.5	6.55
$C_6H_5CH_2Cl$	2.70×10^3	1.39×10^3
$C_6H_5CH_2Br$		9.2×10^3 ^{b}
$Br(CH_2)_2Br$		7.75
$Br(CH_2)_4Br$		2.55

[a] At 25 °C, [H$^+$] = 10^{-2} M, and μ = 0.5 M (HClO$_4$ + LiClO$_4$). [b] In 1:1 CH$_3$CN/H$_2$O, [H$^+$] = 5 × 10^{-3} M, μ = 0.050 M (Bakac, A.; Espenson, J. H. *J. Chem. Soc., Chem. Commun.* **1990**, 1646).

Kinetics. All the reactions obeyed a mixed second-order rate law of eq 2. A summary of all the rate constants is given in Table II. The reactivity order, CH$_3$ < primary alkyl < secondary alkyl < benzyl, is typical for one-electron processes.[15,16,18,23]

$$-d[(H_2O)_2CrL^{2+}]/2\,dt = -d[RX]/dt = k_{RX}[(H_2O)_2CrL^{2+}][RX] \quad (2)$$

Decomposition of (H$_2$O)LCrR^{2+}. The organochromium complexes are stable in solution for at least several hours for R = CH$_3$ and primary alkyl, but the isopropyl complex decomposes readily. For example, a solution containing 0.18 mM (H$_2$O)LCrCH(CH$_3$)$_2^{2+}$ and 3 mM (CH$_3$)$_2$CHBr at 0.01 M HClO$_4$ (μ = 0.5 M) decomposes with $k = 6 \times 10^{-4}$ s^{-1}. The reaction yields propane and propene in a 3:1 ratio, which does not change even when the reaction is conducted in the presence of a large excess of (H$_2$O)$_2$CrL^{2+} ([(H$_2$O)LCrCH(CH$_3$)$_2^{2+}$] = 0.5 mM, [(H$_2$O)$_2$CrL^{2+}] = 4 mM), suggesting that two processes are taking place under these conditions. The source of propane is probably the acidolysis, eq 3, a process that has been well documented in the pentaaquaalkylchromium series.[27]

$$(H_2O)LCrCH(CH_3)_2^{2+} + H^+/H_2O \xrightarrow{k_a} (H_2O)_2CrL^{3+} + C_3H_8 \quad (3)$$

The source of propene appears to be the β-elimination of eq 4. We rule out the Cr–C bond homolysis followed byradical self-reactions as a source of propene, since no (CH$_3$)$_2$CHCH(CH$_3$)$_2$ was found. If the free 2-propyl radicals had been involved, then the yield of (CH$_3$)$_2$CHCH(CH$_3$)$_2$ would be ~45% of the total radical concentration.[28]

$$(H_2O)LCrCH(CH_3)_2^{2+} \xrightarrow{k_\beta} (H_2O)LCrH^{2+} + C_3H_6 \quad (4)$$

The hydridochromium product of eq 4 would decompose rapidly in acidic solutions to yield (H$_2$O)$_2$CrL^{3+} (eq 5).[29]

$$(H_2O)LCrH^{2+} + H^+/H_2O \rightarrow (H_2O)_2CrL^{3+} + H_2 \quad (5)$$

In the presence of 2 mM (NH$_3$)$_5$CoCl^{2+}, a scavenger for both (H$_2$O)$_2$CrL^{2+} and 2-propyl radicals, the decomposition rate of (H$_2$O)LCrCH(CH$_3$)$_2^{2+}$ increases to $k \sim 3.5 \times 10^{-3}$ s^{-1}. The main organic product is 2-propyl chloride, indicating that Cr–C bond homolysis dominates under these conditions (eqs 6–8).

$$(H_2O)LCrCH(CH_3)_2^{2+} \overset{H_2O,\ k_{hom}}{\rightleftarrows} (H_2O)_2CrL^{2+} + {}^{\bullet}CH(CH_3)_2 \quad (6)$$

$$(H_2O)_2CrL^{2+} + (NH_3)_5CoCl^{2+} \xrightarrow{k_{Co},\ 5H^+} (H_2O)LCrCl^{2+} + Co^{2+} + 5NH_4^+ \quad (7)$$

$${}^{\bullet}CH(CH_3)_2 + (NH_3)_5CoCl^{2+} \xrightarrow{k_R,\ 5H^+} ClCH(CH_3)_2 + Co^{2+} + 5NH_4^+ \quad (8)$$

Discussion

The reactions of (H$_2$O)$_2$Cr([14]aneN$_4$)$^{2+}$ and alkyl halides, studied in this work, parallel in all the major respects the reduction of alkyl halides by other one-electron metal reductants, such as Cr([15]aneN$_4$)(H$_2$O)$_2^{2+}$,[15] Ni(tmc)$^+$,[18] and Co(CN)$_5^{2-}$.[23] All these reactions take place with a 2:1 (reductant:RX) stoichiometry and yield 1 mol of alkylmetal and 1 mol of metal halide/mol of RX. The trend in the reactivity of alkyl halides is also the same for all four complexes: methyl < primary < secondary ~ benzyl; I > Br > Cl. All the observations are fully consistent with a sequence shown in eqs 9–11.

$$RX + M \xrightarrow{k_{RX}} MX + R \quad (9)$$

$$R + M \rightarrow RM \quad (10)$$

$$\text{overall:}\quad 2M + RX \rightarrow MX + MR \quad (11)$$

The intermediacy of radicals has been demonstrated in several cases,[15,16,23] and the formation of MX is a clear indication that the radical-forming step involves halogen atom abstraction and not outer-sphere electron transfer. The substitutional inertness of chromium(III) and cobalt(III) would preclude the formation

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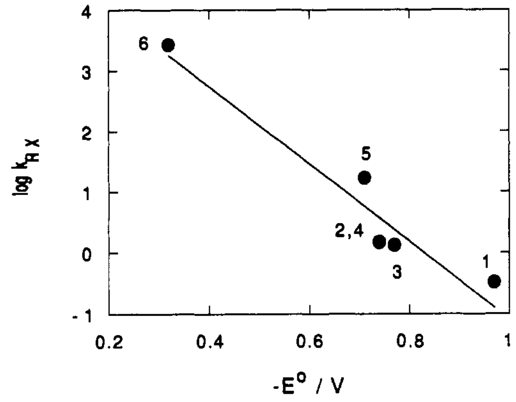

Figure 2. Plot of the logarithm of the rate constant for the reaction of $(H_2O)_2Cr([14]aneN_4)^{2+}$ with alkyl halides versus the reduction potentials of the alkyl halides: CH_3I (1), C_2H_5Br (2), 1-C_3H_7Br (3), 1-C_4H_9Br (4), 2-C_3H_7Br (5), $C_6H_5CH_2Cl$ (6).

of the observed halometal complexes had the reaction yielded free halide ions and the trivalent metal complexes as initial products.

The abstraction of halogen atoms from alkyl halides by alkyl and aryl radicals proceeds through a polar transition state.[30] This was shown by Hammett and Taft correlations that have positive ρ values, suggesting the development of negative charge on the carbon from which halogen is removed.[30]

One should expect the same type of charge separation to take place in halogen abstractions by metal complexes as well. The effect of solvent on the kinetics of RX reduction by $(H_2O)_2CrL^{2+}$ supports this notion. The faster reaction in the more polar H_2O than in 1:1 *tert*-butyl alcohol/H_2O is consistent with the charge development and/or separation in the transition state, as shown in eq 12.

$$RX + CrL^{2+} \rightarrow [R^{\delta-}\text{--}X\text{--}Cr^{\delta+}L] \rightarrow R^{\bullet} + XCrL^{2+} \qquad (12)$$

We note a linear correlation between the reduction potentials of RX and the rate constants for the reaction with $(H_2O)_2CrL^{2+}$ (Figure 2). Even though the reaction takes place by atom transfer and not electron transfer, the driving force within the series is still expected to influence the kinetics of the overall reaction. According to the generalized Marcus theory, the rate constant for atom or group transfer is related to the rate constants for the identity reactions, eqs 13 and 14,and to the equilibrium constant

$$RX + R^{\bullet} \rightleftharpoons R^{\bullet} + RX \qquad (13)$$

$$(H_2O)_2CrL^{2+} + (H_2O)LCrX^{2+} \rightleftharpoons (H_2O)LCrX^{2+} + (H_2O)_2CrL^{2+} \qquad (14)$$

$$(H_2O)_2CrL^{3+} + X^- \overset{K_X}{\rightleftharpoons} (H_2O)LCrX^{2+} + H_2O \qquad (15)$$

for the cross-reaction of eq 9.[31] The equilibrium constant K_9 is in turn a function of the reduction potentials for the $RX/(R^{\bullet} + X^-)$ and $(H_2O)_2CrL^{3+/2+}$ couples and of the equilibrium constant K_X for the binding of X^- to $(H_2O)_2CrL^{3+}$. Thus, for a series of reactions with a common reductant, one expects a linear correlation between the rates and potentials, since other parameters either are constant or are expected to vary smoothly throughout the series. A more detailed analysis of the data cannot be carried out, however, since neither the identity rate constants nor the binding constants K_X are available for the reactants studied.

The decomposition of $(H_2O)LCrCH(CH_3)_2^{2+}$ takes place by at least three parallel pathways: acidolysis, β-elimination, and homolysis. This is clearly demonstrated by the effect of $(NH_3)_5CoCl^{2+}$ on the decomposition kinetics and by the nature of the products formed. A detailed investigation of the decomposition process, including kinetics, products, and the trapping of intermediates, is under way for several $(H_2O)LCrR^{2+}$ complexes.

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