cherche Scientifique (Grant No. 20-28470-90) for financial support.

Registry No. **1**, 136630-30-3; **2**, 136630-31-4; **3**, 136630-28-9; **4**·CH_3COOH, 136658-69-0; **5**, 136630-29-0; $WOCl_4$, 13520-78-0; WCl_6, 13283-01-7; *p-tert*-butylcalix[4]arene, 60705-62-6.

Supplementary Material Available: For **4** and **5**, ORTEP projections of the complexes and their unit cells and complete listings of crystallographic data, fractional atomic coordinates for hydrogen atoms, anisotropic thermal parameters, and bond distances and angles (14 pages); listings of observed and calculated structure factors (52 pages). Ordering information is given on any current masthead page.

Contribution from Ames Laboratory and
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Oxidative Homolysis Reactions between Organochromium Macrocycles and Dihalide Radical Anions

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Many electron acceptors are able to oxidize organometals. In the case of organochromium(III) complexes such as $(H_2O)_5CrR^{2+}$ and $RCrL(H_2O)^{2+}$ (L = [15]aneN_4 = 1,4,8,12-tetraazacyclopentadecane), studies of the oxidation step have been examined as in eq 1 for the acceptors $Ru(bpy)_3{}^{3+}$, ${}^2E$-$Cr(bpy)_3{}^{3+}$, Ni([14]aneN_4)$^{3+}$, and $IrCl_6{}^{2-}$.[2-4]

$$CrR^{2+} + A \rightarrow CrR^{3+} + A^- \qquad (1)$$

Indeed, although I_2 is a very weak acceptor, reaction 1 for $RCrL(H_2O)^{2+}$ complexes produces enough $RCrL^{3+}$, and then by its homolysis, enough $R^\bullet$ is formed to initiate a chain sequence for the electrophilic cleavage of the chromium–carbon bond by iodine.[5] As a result of the reaction between $R^\bullet$ and I_2, $I^\bullet$ is formed and thus $I_2{}^{\bullet-}$. The form of the rate law for the reaction between I_2 and $RCrL(H_2O)^{2+}$ allowed us to infer that one of the chain-propagating steps was the oxidation of the organometal by $I_2{}^{\bullet-}$:

$$I_2{}^{\bullet-} + RCrL(H_2O)^{2+} \rightarrow 2I^- + RCrL(H_2O)^{3+} \qquad (2)$$

The study of the I_2 reaction did not give a value of this rate constant, because *k* for the chain reaction is a composite that contains also the rate constants for the initiation and termination steps.

We decided to investigate reaction 2 for several reasons. First, we wanted to confirm that such a reaction occurs rapidly enough for it to be a chain propagation step in the iodine reaction. Second, we wanted to use its rate constant, in conjunction with the observed constant for the chain reaction, to calculate the rate constant for other elementary steps in the chain. Third, by variation of the group R and by use of other $X_2{}^{\bullet-}$ radicals, we sought to learn more about the nature of the rate-determining step in the reaction. The point behind the use of the macrocycle is that, in donating considerable electron density to the metal, it assists oxidative pathways (for X_2 and $X_2{}^{\bullet-}$) and decreases solvolytic and homolytic decomposition pathways.

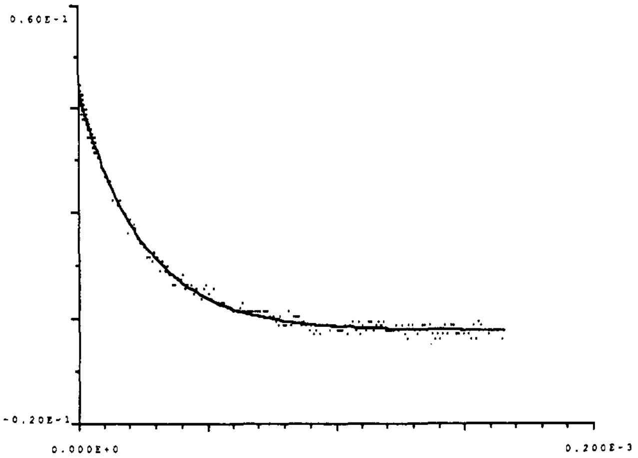

Figure 1. Kinetic trace showing the decay of $Br_2{}^{\bullet-}$ at 400 nm. The radical was generated by pulse radiolysis in N_2O-saturated solution. This is the reaction with 4-$CH_3C_6H_4CH_2Cr$([15]aneN_4)$(H_2O)^{2+}$ at 2.5 × 10^{-4} M. The solid curve was calculated from a nonlinear first-order fitting program. The vertical axis shows absorbance, and the horizontal time in seconds.

Experimental Section

The organochromium complexes were prepared[6,7] from the reaction of organic halide and $(H_2O)_2CrL^{2+}$ for the R groups 4-$BrC_6H_4CH_2$, 4-$CH_3C_6H_4CH_2$, $C_2H_5CH_2$, and $(CH_3)_2CH$. The complexes were separated and purified by ion-exchange chromatography, and their concentrations were determined spectrophotometrically.

The dihalide reagents $X_2{}^{\bullet-}$ (X = I, Br, SCN) were generated by pulse radiolysis of N_2O-saturated solutions of sodium halides or sodium thiocyanate. Hydrated electrons were converted to hydroxyl radicals by reaction with N_2O; the $[H^+]$ was 10^{-4} M so this reaction occurred rather than H atom formation. The reaction of $HO^\bullet$ with X^- forms the desired $X_2{}^{\bullet-}$ species. Ionic strength was maintained with sodium perchlorate. The Argonne electron beam has a 15-MeV energy and a 4-ns pulse length. The reactions were followed by monitoring the disappearance of $X_2{}^{\bullet-}$ at 340, 370, 400, or 475 nm as required. The cell path was 1 or 2 cm as needed to detect $X_2{}^{\bullet-}$ yet minimize the background absorption of the organochromium complex.

The reactions were conducted so as to generate a small burst of $X_2{}^{\bullet-}$ in the presence of a much larger concentration of $RCrL(H_2O)^{2+}$. The disproportionation of the radical (eq 3) contributes to the signal, although

$$2X_2{}^{\bullet-} \rightarrow X^- + X_3{}^- \qquad (3)$$

it is a minor component. It contributed typically 5% at the start of a reaction and progressively less as it proceeded. The kinetic data conformed to first-order kinetics; the data were fit by a nonlinear least-squares equation. A typical kinetic trace, and the first-order fit, are shown in Figure 1.

Results and Discussion

The kinetic experiments had concentrations of the organochromium(III) complexes in the range 10^{-4}–10^{-3} M. The pseudo-first-order rate constants observed were between 9 × 10^3 and 8 × 10^4 s^{-1}. The rate constants were independent of the wavelength of observation. That such a fast decay occurs is consistent with a reaction between $RCrL(H_2O)^{2+}$ and $I_2{}^{\bullet-}$, as suggested from the data on the I_2 chain reaction.

The variation of k_{obs} with $[RCrL(H_2O)^{2+}]$ is linear. These lines have small intercepts corresponding to eq 3 and slopes that are the bimolecular rate constants for the desired $X_2{}^{\bullet-}$ reactions. These values are summarized in Table I, along with the oxidation potentials of the $X_2{}^{\bullet-}$ radicals.[8-11] The two complexes whose re-

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(1) (a) Iowa State University. (b) Ben-Gurion University. (c) Argonne National Laboratory.

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Table I. Rate Constants for the Reactions between $RCrL(H_2O)^{2+}$ Ions and Various Oxidizing Agents[a]

		R			
A	$E_A°/V$[b]	$4\text{-}CH_3C_6H_4CH_2$	$4\text{-}BrC_6H_4CH_2$	$CH(CH_3)_2$	$CH_2C_2H_5$
$Br_2^{\bullet-}$	1.62	9.8×10^7	4.8×10^7	1.8×10^8	2.7×10^7
$(SCN)_2^{\bullet-}$	1.32	4.9×10^7	2.3×10^7	8.0×10^7	1.3×10^7
$I_2^{\bullet-}$	1.03	8.4×10^6		3.7×10^7	
$^2E\text{-}Cr(bpy)_3^{3+}$[c]	1.46	1.55×10^9	1.41×10^9	1.08×10^8	1.17×10^7
$Ru(bpy)_3^{3+}$[c]	1.26[d]	1.05×10^9	4.27×10^8	4.74×10^6	3.50×10^3

[a] At ambient temperature (23 ± 1 °C), pH 4, $\mu = 0.1$ M. L = 1,4,8,12-tetraazacyclopentadecane; k in units L mol^{-1} s^{-1}. [b] Reference 11. [c] Reference 2. [d] Sutin, N.; Creutz, C. *Adv. Chem. Ser.* **1978**, *No. 168*, 1.

actions with $I_2^{\bullet-}$ would have been the slowest were not studied because, at the $[RCrL(H_2O)^{2+}]$ available, reaction 3 would have been dominant.

The rate constants for a given organochromium cation change in order of the driving force, with k's increasing in the series $I_2^{\bullet-} < (SCN)_2^{\bullet-} < Br_2^{\bullet-}$. The rates also respond in a regular way as the group R is varied, decreasing in the sequence $(CH_3)_2CH > 4\text{-}CH_3C_6H_4CH_2 > 4\text{-}BrC_6H_4CH_2 > C_2H_5CH_2$. The same reactivity order was found[2] for oxidations by $^2E\text{-}Cr(bpy)_3^{3+}$ and $Ru(bpy)_3^{3+}$. The rate changes in each series of $X_2^{\bullet-}$ reactions are, however, rather small. That is, reactivity ratios for $Br_2^{\bullet-}$ vs $I_2^{\bullet-}$ are about 10 or less (with the $(SCN)_2^{\bullet-}$ intermediate), and those between the extremes of reactivity of R groups vary only by a factor of 4. In contrast, variation of R gives a factor of 10^2 for $^2E\text{-}Cr(bpy)_3^{3+}$ and $10^{5.4}$ for $Ru(bpy)_3^{3+}$.

It seems particularly significant that the $X_2^{\bullet-}$ reagents do not differ more in rates, given that the extremes of driving force differ by 0.59 V. If self-exchange rates are similar, this would lead to a much larger factor in reactivity between $Br_2^{\bullet-}$ and $I_2^{\bullet-}$ expected by virtue of the Marcus cross relation.[8] The following self-exchange rates have been determined:[9] $(SCN)_2^{\bullet-}/2SCN^-$, 4.6×10^2 L mol^{-1} s^{-1}, and $I_2^{\bullet-}/2I^-$, 1.0×10^3 L mol^{-1} s^{-1}. A value for $Br_2^{\bullet-}/2Br^-$ has not been reported. The values given support the assumption made, and we thus seek a different explanation for the similarity in rates. According to the Marcus equation, a difference of 10^{10} in the equilibrium constant should translate, by a square root factor, to 10^5 in reactivity. This suggests that the rate-limiting step in the $X_2^{\bullet-}$ reactions is not purely electron transfer. We thus consider a mechanism (eqs 4 and 5) in which a loosely bound adduct is involved.

$$X_2^{\bullet-} + RCrL(H_2O)^{2+} \rightleftarrows \{X_2^-, RCrL(H_2O)^{2+}\} \qquad (k_4, k_{-4}) \tag{4}$$

$$\{X_2^-, RCrL(H_2O)^{2+}\} \rightarrow 2X^- + RCrL(H_2O)^{3+} \qquad (k_5) \tag{5}$$

In this scheme the experimental rate constant k is given by

$$k = \frac{k_4}{1 + (k_{-4}/k_5)} \tag{6}$$

If k_5 is, indeed, responsive to driving force, then its effect can be muted if k_{-4} is relatively large. This implies an adduct unstable toward dissociation. While one cannot rule out the formulation of this adduct as an ion pair, we are more inclined to believe that it represents an interaction between $X_2^{\bullet-}$ and the α-carbon of the alkyl group bound to chromium. This is because (1) no ion pairs are found with oxidants ranging in charge from 2− ($IrCl_6^{2-}$)[4] to 3+ ($Ru(bpy)_3^{3+}$)[2] and (2) the response as R is varied is much less for each of the $X_2^{\bullet-}$ radicals than for $^2E\text{-}Cr(bpy)_3^{3+}$ and $Ru(bpy)_3^{3+}$. The interaction of $X_2^{\bullet-}$ with $RCrL(H_2O)^{2+}$ may be related to the polarizing ability of halogens. Although direct attack of $X_2^{\bullet-}$ may thus not occur at the α-carbon of an alkylmetal, it is a well-documented pathway for X_2. It may simply be that with I_2 and other X_2's the products of two-electron substitutions predominate (i.e., X^-, RX, and $(H_2O)_2CrL^{3+}$), whereas with the one-electron radical ion electron-transfer products are formed (e.g. $2X^-$, $RCrL(H_2O)^{3+}$). The oxidized organochromium ion persists for a short but undetermined period of time beyond its formation in eq 5, since it can be captured by other reagents.[2]

We shall now consider the significance of these findings for the mechanism of the iodinolysis reactions. Under suitable conditions, and in the absence of chain inhibitors, the kinetic data are consistent with a chain mechanism initiated by electron transfer (eq 7), propagated by reactions in which $R^\bullet$ and $X_2^{\bullet-}$ are the chain-carrying intermediates (eqs 8–11), and terminated by disproportionation of $I_2^{\bullet-}$ (eq 12).

$$I_2 + RCrL(H_2O)^{2+} \rightarrow I_2^{\bullet-} + RCrL(H_2O)^{3+} \tag{7}$$

$$RCrL(H_2O)^{3+} + H_2O \rightarrow R^\bullet + (H_2O)_2CrL^{3+} \tag{8}$$

$$R^\bullet + I_2 \rightarrow RI + I^\bullet \tag{9}$$

$$I^- + I^\bullet \rightleftarrows I_2^{\bullet-} \tag{10}$$

$$I_2^{\bullet-} + RCrL(H_2O)^{2+} \rightarrow 2I^- + RCrL(H_2O)^{3+} \tag{11}$$

$$2I_2^{\bullet-} \rightarrow I_2 + 2I^- \tag{12}$$

The experimental rate law has the form

$$-d[RCrL(H_2O)^{2+}]/dt = k_{\text{exptl}}[I_2]^{1/2}[RCrL(H_2O)^{2+}]^{3/2} \tag{13}$$

According to the scheme shown, $k_{\text{exptl}} = k_{11}(k_7/k_{12})^{1/2}$. Accurate data were obtained[5] only for the case R = $4\text{-}BrC_6H_4CH_2$, where $k_{\text{exptl}} = 18.3$ L mol^{-1} s^{-1}. With $k_{11} \sim 4 \times 10^6$ L mol^{-1} s^{-1} (interpolated in Table I), and $k_{12} = 4.5 \times 10^9$ L mol^{-1} s^{-1},[10] a value can be calculated for $k_7 = 9 \times 10^{-2}$ L mol^{-1} s^{-1}. This value is some 7 orders of magnitude smaller than the rate constant for oxidation by $I_2^{\bullet-}$ (k_{11}). The one-electron potentials[11-13] of I_2(aq) (0.21 V)[10-12] and $I_2^{\bullet-}$ (1.03 V) together with the self-exchange rates[9,14,15] of the partners $I_2/I_2^{\bullet-}$ and $I_2^{\bullet-}/2I^-$ can be considered. These data allow the estimation of the ratio $k_{11}/k_7 = 1 \times 10^6$, by use of the Marcus cross relation.

First, we note that it is a large number, consistent with $I_2^{\bullet-}$ being in general a much more reactive oxidizing agent than I_2. Second, it is lower than the experimental ratio of 4×10^7. Let us assume that the discrepancy lies in k_{11} and not k_7. If so, k_{11}(exptl) = 4×10^6 and k_{11}(theor) = 9×10^4 L mol^{-1} s^{-1}. The larger experimental value may again signal a mechanism that is not simple electron transfer, which is the implication of the suggested mechanistic steps of eqs 4 and 5. In that mechanism $k < k_4$, as in eq 6.

Finally, we compare k_7 with the rate constant for another pathway by which I_2 reacts with an organochromium complex, the electrophilic substitution step shown in eq 14. For R =

$$I_2 + RCrL(H_2O)^{2+} \xrightarrow{H_2O} (H_2O)_2CrL^{3+} + RI + I^- \tag{14}$$

$4\text{-}BrC_6H_4CH_2$, $k_{14} = 9.5$ L mol^{-1} s^{-1}.[5] This is clearly much larger than that for the electron-transfer step, for which $k_7 = 9 \times 10^{-2}$ L mol^{-1} s^{-1}. Which reaction actually predominates, however, depends also on the reactant concentrations, since the rate laws are of different form and since the effective constant for the electron-transfer chain is not simply k_7 but the composite shown in eq 13. Also, if chain-breaking reagents are added, such as Fe^{2+},

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Cu^{2+}, or O_2, then the chain is suppressed to the extent that the electrophilic pathway emerges, which was the method by which k_{14} was evaluated.

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Registry No. 4-$CH_3C_6H_4CH_2CrL(H_2O)^{2+}$, 129834-70-4; 4-$BrC_6H_4CH_2CrL(H_2O)^{2+}$, 125329-98-8; $(CH_3)_2CHCrL(H_2O)^{2+}$, 70833-00-0; $C_2H_5CH_2CrL(H_2O)^{2+}$, 70832-98-3; $Br^{\bullet-}$, 12595-70-9; $(SCN)_2^{\bullet-}$, 34504-17-1; $I_2^{\bullet-}$, 12190-71-5.

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Kinetic and Thermodynamic Acidity of Hydrido Transition-Metal Complexes. 9.[1] A Sterically Hindered Cationic Hydride, $[H_4Re(PMe_2Ph)_4]^+$

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Cationic polyhydride complexes $MH_xL_y^+$ can adopt either a classical structure with individual hydride ligands or a nonclassical one, $M(\eta^2\text{-}H_2)H_{x-2}L_y^+$, with two hydrogens coordinated as a dihydrogen molecule.[2] While there has been considerable interest[3,4] in the relative acidity of dihydride cations and the corresponding η^2-H_2 complexes, only one dihydrogen complex, $CpRu(dmpe)(\eta^2\text{-}H_2)^+$,[3] has had its *thermodynamic* acidity measured in acetonitrile (the solvent we have found[1a,b] best suited for determining the thermodynamic acidity of transition-metal hydrides); no classical polyhydride cation has been examined in that solvent.[5] Furthermore, in no case has the *kinetic* acidity (k_{H^+} in eq 1) of a cationic polyhydride complex been measured

$$H\text{-}M + PhNH_2 \underset{k_b}{\overset{k_{H^+}}{\rightleftharpoons}} M^- + PhNH_3^+ \qquad (1)$$

in acetonitrile with aniline (the base we have used[1a,b,6] to compare the kinetic acidity of an extensive series of transition-metal hydrides). Finally, neither the thermodynamic nor the kinetic acidity of a *congested* hydride has ever been examined in acetonitrile; our previous studies[1,6] have involved relatively uncrowded complexes with carbonyl ligands.

Table I. Determination of the Acetonitrile pK_a of $[H_4Re(PMe_2Ph)_4][BF_4]$ (1)

base (B)	pK_a(BH$^+$)	K_{eq}	pK_a(1)
TMG	23.3[a]	5.66×10^{-3}	25.5
DBU	24.3[b]	7.54×10^{-2}	25.4
$K[OC_6H_5]$	26.6[c]	>0.4	<27

[a] Reference 10a,b,e. [b] Reference 11. [c] Reference 10d,e.

We have therefore quantified the thermodynamic and kinetic acidity of $[H_4Re(PMe_2Ph)_4]^+$ (**1**)[7] in acetonitrile solution. While the related rhenium hydride $[H_4Re(CO)(PMe_2Ph)_3]^+$ (**2**) exists in solution as a mixture of the classical tetrahydride and the nonclassical (η^2-H_2) dihydride tautomers[8] and the iridium analogue $[H_4Ir(PMe_2Ph)_3]^+$ (**3**) is entirely nonclassical, with two dihydride ligands and a labile dihydrogen ligand,[9] Caulton and co-workers have shown[7] **1** to exist in solution as the classical tetrahydride isomer only. Furthermore, while **2** and **3** are deprotonated by triethylamine in CH_2Cl_2,[8,9a] Caulton and co-workers have also found[7] that **1** is not deprotonated by triethylamine in that solvent.

Experimental Section

All manipulations were carried out using Schlenk, high-vacuum, or inert-atmosphere-box techniques. CD_3CN was dried over P_2O_5 and degassed by repeated freeze/pump/thaw cycles. Aniline-d_2 was generated by shaking aniline with D_2O 10 times, followed by fractional distillation from BaO and vacuum transfer prior to use; deuterium incorporation was 95%. $DNBu_2$ was prepared in the same way and dried and stored over 3-Å molecular sieves. The neutral parent complex of **1**, $H_3Re(PMe_2Ph)_3$ (**4**), was generously donated by Prof. K. G. Caulton, Indiana University, and converted to **1** by protonation with $HBF_4{\cdot}OEt_2$.[7]

CD_3CN solutions of **1** and various bases were sealed under vacuum and their ^1H NMR spectra recorded on either an IBM WP-200-SY or an IBM WP-270-SY spectrometer. Concentrations of all species involved were determined by integration of ^1H peaks relative to $(Me_3Si)_2O$ as an internal standard. Since a very small amount of $(Me_3Si)_2O$ was needed, it was quantified by gas volume measurements (typically 1.05 mL at 30 mmHg and 23 °C, or 1.89×10^{-6} mol).

Results and Discussion

Thermodynamic Acidity. The inability of Et_3N to deprotonate **1** in CH_2Cl_2 suggested that a stronger base than Et_3N would be required to do so in acetonitrile. Preliminary experiments in CD_3CN showed no deprotonation of **1** with 8 equiv of tetramethylguanidine (TMG), a base whose conjugate acid has a CH_3CN pK_a of 23.3[10a,b,e] (the CH_3CN pK_a of Et_3NH^+ is 18.5[10c,e]). In contrast, potassium phenolate (the CH_3CN pK_a of PhOH is 26.6[10d,e]) completely deprotonated **1**. The use of conditions more basic than 8 equiv of TMG but less basic than phenolate was thus indicated, and the required partial deprotonation of **1** was effected by 60 equiv of TMG or 5 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) ($DBUH^+$ has a CH_3CN pK_a of 24.3[11]).

The concentrations of **1** and its conjugate base **4** in the presence of each base B (eq 2) were determined by integration of the

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(5) The CH_3CN pK_a of $CpRu(dmpe)(H)_2^+$ could be computed from the pK_a (17.6)[3] of the corresponding dihydrogen complex and the equilibrium constant for interconversion of the two tautomers in CH_3CN,[1b] but the equilibrium constant is not reported in that solvent in ref 3. The lability of most dihydrogen complexes makes it difficult to determine their pK_a in a coordinating solvent,[4] so the pK_a of **3** surely, and that of a tautomeric mixture like **2** probably, cannot be measured in CH_3CN.

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