

Kinetic method to estimate the reduction potential involving unstable organochromium macrocyclic complex

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Abstract

The complex $[4\text{-BrC}_6\text{H}_4\text{CH}_2\text{Cr}(1,4,8,12\text{-tetraazacyclopentadecane})(\text{H}_2\text{O})]^{2+}$, $(\text{RCrL}(\text{H}_2\text{O})^{2+})$ is oxidized to $\text{RCrL}(\text{H}_2\text{O})^{3+}$ which then rapidly homolyses. The rate constants were determined in aqueous solution at 25.0°C for oxidation by IrCl_6^{2-} and 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulphonate) monoanion, $(\text{ABTS}^{\bullet-})$; the values are $(1.29 \pm 0.11) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $(1.51 \pm 0.17) \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ respectively. The estimates of reduction potential E^0 and self-exchange rate constant k_{11} were made for the couple $4\text{-BrC}_6\text{H}_4\text{CH}_2\text{CrL}(\text{H}_2\text{O})^{3+/2+}$: $E^0 = 0.8 \pm 0.2 \text{ V}$; $5 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} < k_{11} < 7 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Key words: Chromium; Macrocyclic; Kinetics; Electron transfer

1. Introduction

Transition metal complexes containing metal-carbon bonds are involved in various oxidation mechanisms [1]. Unlike inorganic complexes, where the metal may exist in two or more stable oxidation states, a one-electron oxidation of an organometal RM often yields an unstable species RM^+ which readily decomposes by homolysis: $\text{RM}^+ \rightarrow \text{R}^{\bullet} + \text{M}^+$. The series of complexes $(\text{H}_2\text{O})_5\text{CrR}^{2+}$ is oxidized by strong one-electron acceptors such as $\text{Ni}(\text{cyclam})^{3+}$ ($E^0 = 1.0 \text{ V}$), $\text{Ru}(\text{bpy})_3^{3+}$ ($E^0 = 1.27 \text{ V}$) and NO^+ ($E^0 = 1.51 \text{ V}$), yielding $(\text{H}_2\text{O})_5\text{CrR}^{3+}$ which quickly decomposes into $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ and organic products derived from R^{\bullet} [2–4].

Replacement of four water molecules in $(\text{H}_2\text{O})_5\text{CrR}^{2+}$ by a macrocyclic ligand L ($\text{L} = 1,4,8,12\text{-tetraazacyclopentadecane}$) lowers the reduction potential of the complex and hence causes the Cr-C bond to become more susceptible to oxidation. Even a mild oxidant such as $\text{I}_2(\text{I}_2(\text{aq})/\text{I}_2^{\bullet-})$; $E^0 = 0.21 \text{ V}$ [5] can oxidize $\text{RCrL}(\text{H}_2\text{O})^{2+}$ ($\text{R} = \text{ArCH}_2$ or 2^0-alkyl) to the extent to initiate a radical chain reaction [6]:



The relatively low reduction potentials of the macrocyclic organochromium complexes offers certain advantages in studying the electron transfer reaction concerning the Cr-C bond.

One of the challenging problems is to obtain the $\text{RCrL}(\text{H}_2\text{O})^{3+/2+}$ reduction potential E^0 and self-exchange rate (SER) constant k_{11} , which is difficult owing to the instability of $\text{RCrL}(\text{H}_2\text{O})^{3+}$. The approach suggested here is based on kinetic methodology. It uses two oxidants for a given $\text{RCrL}(\text{H}_2\text{O})^{2+}$ complex to estimate the E^0 and k_{11} values.

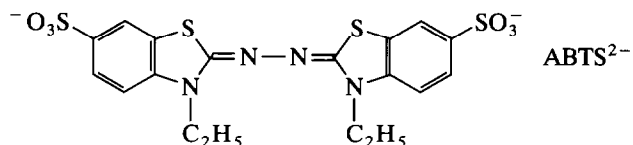
The two oxidants were chosen such that one is weak (2,2'-azino-bis(3-ethylbenzthiazoline-6-sulphanate) ($\text{ABTS}^{\bullet-}/2^-$); $E^0 = 0.43 \text{ V}$) [7] and the other strong ($\text{IrCl}_6^{2-}/3^-$; $E^0 = 0.89 \text{ V}$) [8]. With the weak oxidant, the retarding effect (of ABTS^{2-}) can be measured, and a lower limit can be set for the kinetic lifetime of the purported product, $\text{RCrL}(\text{H}_2\text{O})^{3+}$, based on the magnitude of the retardation. An upper limit of the lifetime of $\text{RCrL}(\text{H}_2\text{O})^{3+}$ can be set by the reaction rate of $\text{RCrL}(\text{H}_2\text{O})^{2+}$ with the strong oxidant. A combination of these limits allows an estimate of E^0 . From the Marcus [9] equation, the SER constant k_{11} of the $\text{RCrL}(\text{H}_2\text{O})^{3+/2+}$ couple can then be calculated.

2. Experimental section

2.1. Materials

The complex $4\text{-BrC}_6\text{H}_4\text{CH}_2\text{CrL}(\text{H}_2\text{O})^{2+}$ was synthesized and purified by methods given in the literature [6]. The concentrations of the complexes in the kinetic studies were calculated from the molar absorp-

tivities at the following wavelengths: 245 nm ($\epsilon = 1.07 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), 281 nm ($\epsilon = 9.82 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), 303 nm ($\epsilon = 8.83 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and 361 nm ($\epsilon = 2.40 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) [6]. The radical ion $\text{ABTS}^{\bullet-}$ was generated by oxidation of $(\text{NH}_4)_2\text{ABTS}$ (Aldrich) with an equivalent amount of $(\text{NH}_4)_2\text{Ce}(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$ (Sigma) and the structural formula of ABTS^{2-} is as follows:



The radical $\text{ABTS}^{\bullet-}$ persists in solutions for several weeks; it is characterized by a number of UV-visible absorption bands of which the peak at 660 nm ($\epsilon = 1.20 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) [10] was used to follow its reactions. Sodium hexachloroiridate(IV) trihydrate, $\text{Na}_2\text{IrCl}_6 \cdot 3\text{H}_2\text{O}$, was purchased from Aldrich and used without further purification. Its concentration was determined spectrophotometrically at both 487 nm ($\epsilon = 4.05 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and 460 nm ($\epsilon = 2.08 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) [11], and its reaction with the organochromium complexes $\text{RCrL}(\text{H}_2\text{O})^{2+}$ was monitored at 487 nm.

2.2. Techniques and kinetics

Kinetic measurements were conducted in aqueous solutions at 25°C with $[\text{H}^+] = 1.0 \times 10^{-2} \text{ M}$ (perchloric acid) and ionic strength 0.20 M (maintained with sodium perchlorate). In the controlled experiments, a variation in $[\text{H}^+]$ (pH 2–3) was employed whereas the ionic strength of 0.20 M was maintained. Air-free conditions were maintained in all experiments by a blanket of argon. Kinetic data were collected with a Durrum-Dionex stopped-flow spectrophotometer controlled by the On Line Instrument Systems data acquisition and analysis software. Kinetic data were analysed by a non-linear least-squares fitting to the equation $D_t = D_\infty + (D_0 - D_\infty) \exp(-k_\psi t)$.

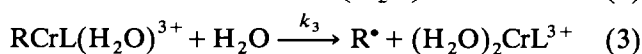
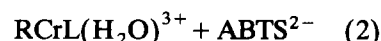
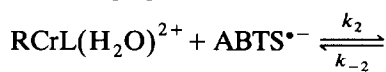
2.3. Cyclic voltammetry

A three-electrode one-compartment cell was connected to a BAS 100 electrochemical analyser for cyclic voltammetric measurements. An Ag/AgCl electrode was used as reference, and a Pt wire as auxiliary. Both glassy carbon electrodes (with diameters of 1 mm and 4 mm respectively) and Pt disc electrode (4 mm diameter) were employed as working electrode. All the electrochemical experiments were conducted in a 0.1 M Me_4NBF_4 acetonitrile solution under an argon atmosphere.

3. Results and discussion

3.1. Oxidation of $4\text{-BrC}_6\text{H}_4\text{CH}_2\text{CrL}(\text{H}_2\text{O})^{2+}$

In the reaction with $4\text{-BrC}_6\text{H}_4\text{CH}_2\text{CrL}(\text{H}_2\text{O})^{2+}$, the $\text{ABTS}^{\bullet-}$ radical functions both as an oxidizing agent ($E^0 = 0.43 \text{ V}$) [7] and as a radical scavenger [10]. The oxidized organochromium complex [6] $\text{RCrL}(\text{H}_2\text{O})^{3+}$ subsequently undergoes homolysis, with the resulting radical forming an adduct with $\text{ABTS}^{\bullet-}$ in a known reaction [10]:



This scheme requires a stoichiometry of $1\text{RCrL}(\text{H}_2\text{O})^{2+} : 2\text{ABTS}^{\bullet-}$, which is confirmed by spectrophotometric titration (Fig. 1).

The rate equation derived on the basis of reactions (2)–(4), with the steady state approximation for $[\text{RCrL}(\text{H}_2\text{O})^{3+}]$, is

$$\frac{-d[\text{RCrL}(\text{H}_2\text{O})^{2+}]}{dt} = \frac{k_2 k_3 [\text{ABTS}^{\bullet-}] [\text{RCrL}(\text{H}_2\text{O})^{2+}]}{k_3 + k_{-2} [\text{ABTS}^{2-}]} = k_\psi [\text{RCrL}(\text{H}_2\text{O})^{2+}] \quad (5)$$

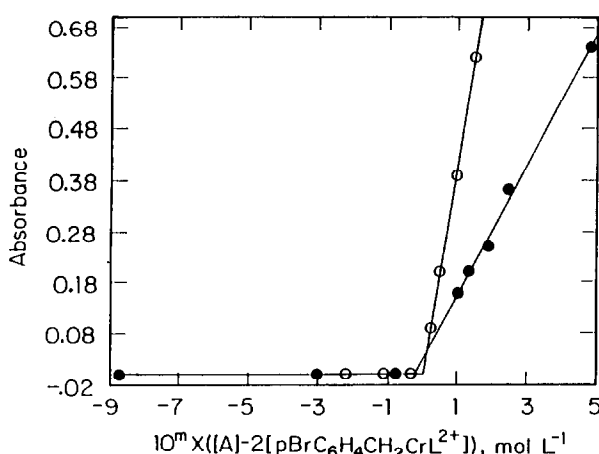


Fig. 1. Spectrophotometric titrations of $4\text{-BrC}_6\text{H}_4\text{CH}_2\text{CrL}(\text{H}_2\text{O})^{2+}$ by electron acceptor A showing 1:2 stoichiometry as in eqns. (2)–(4): ●, $m = 5$, A $\equiv \text{ABTS}^{\bullet-}$, monitored at 660 nm with an optical length of 1 cm; ○, $m = 4$, A $\equiv \text{IrCl}_6^{2-}$, monitored at 487 nm with an optical length of 1 cm.

With $\text{ABTS}^{\bullet-}$ ($(1.2\text{--}12.0) \times 10^{-5}$ M average concentrations) in excess over $4\text{-BrC}_6\text{H}_4\text{CH}_2\text{CrL}(\text{H}_2\text{O})^{2+}$ ($(2.1\text{--}5.9) \times 10^{-6}$ M), and with no added ABTS^{2-} , the expression reduces to $k_\psi = k_2[\text{ABTS}^{\bullet-}]$. This is illustrated in Fig. 2. The average value of k_2 is $(1.53 \pm 0.11) \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in six determinations. A series of seven experiments was then done with added ABTS^{2-} (range of average concentrations 7.0×10^{-6} – 3.39×10^{-4} M) and constant $[\text{ABTS}^{\bullet-}]_{\text{av}}$ (9.32×10^{-5} M). Values of k_ψ become smaller with increasing $[\text{ABTS}^{2-}]$, as expected from eqn. (5). A non-linear least-squares fit to eqn. (5) affords an independent estimate of $k_2 = (1.51 \pm 0.17) \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and the ratio $k_{-2}/k_3 = (6.7 \pm 0.70) \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$. The effect is displayed graphically in Fig. 3 by rearranging eqn. (5) to give

$$k_\psi = k_2[\text{ABTS}^{\bullet-}]_{\text{av}} - \frac{k_{-2}}{k_3} k_\psi [\text{ABTS}^{2-}]_{\text{av}} \quad (6)$$

The oxidation of $4\text{-BrC}_6\text{H}_4\text{CH}_2\text{CrL}(\text{H}_2\text{O})^{2+}$ by IrCl_6^{2-} also proceeds with a 1:2 stoichiometry (Fig. 1). The scheme is analogous to eqns. (2)–(4), except that the fate of the radical is oxidation to a mixture of alcohol and halide [12]:

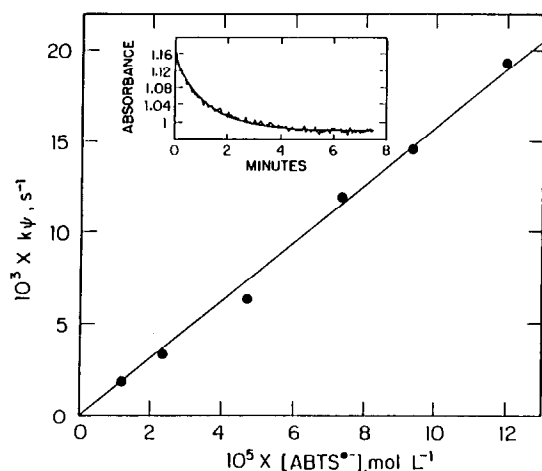
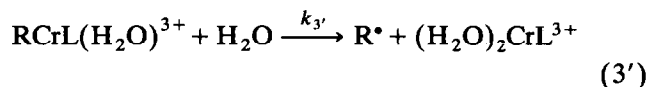
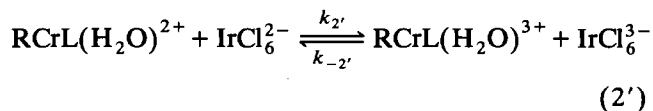


Fig. 2. A plot showing the linear variation in k_ψ with $[\text{ABTS}^{\bullet-}]$ in experiments without added ABTS^{2-} . The inset shows the kinetic trace and the least-squares fit to it, for an experiment with $[\text{ABTS}^{\bullet-}]_0 = 5.0 \times 10^{-5}$ M, $[4\text{-BrC}_6\text{H}_4\text{CH}_2\text{CrL}(\text{H}_2\text{O})^{2+}]_0 = 3.0 \times 10^{-6}$ M, $[\text{H}^+] = 1.0 \times 10^{-2}$ M at $I = 0.20$ M and 25°C , and an optical length of 2 cm.

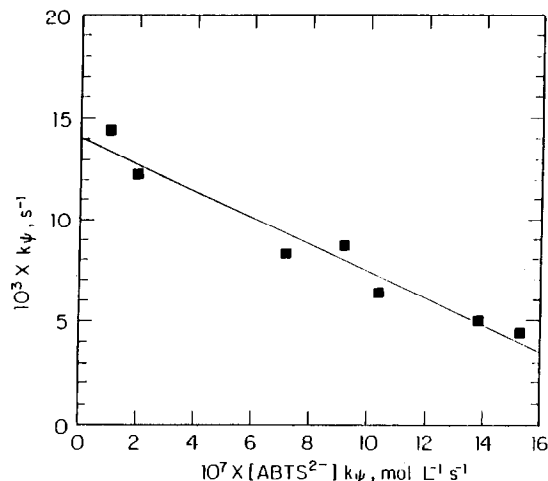
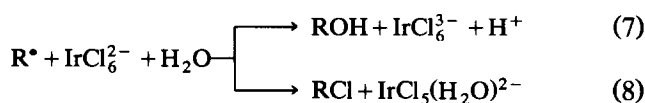


Fig. 3. A plot according to eqn. 6, illustrating the inhibiting effect of added ABTS^{2-} .



Kinetic measurements were conducted with either reagent in tenfold excess. In all, the concentration variations were $[\text{RCrL}(\text{H}_2\text{O})^{2+}]_0 = 1.55 \times 10^{-5}$ – 2.44×10^{-4} M and $[\text{IrCl}_6^{2-}]_0 = 5 \times 10^{-6}$ – 4.5×10^{-4} M in 11 experiments. The reaction obeys a second-order rate law

$$\frac{-d[\text{RCrL}(\text{H}_2\text{O})^{2+}]}{dt} = k_2 [\text{RCrL}(\text{H}_2\text{O})^{2+}] [\text{IrCl}_6^{2-}] \quad (9)$$

with $k_2 = (1.29 \pm 0.18) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Controlled experiments show that reaction rates are independent of added IrCl_6^{3-} concentration over the $(0\text{--}1.0) \times 10^{-3}$ M range and the oxidations of $4\text{-BrC}_6\text{H}_4\text{CH}_2\text{CrL}(\text{H}_2\text{O})^{2+}$ by both $\text{ABTS}^{\bullet-}$ and IrCl_6^{2-} are independent of $[\text{H}^+]$ over the pH 2–3 range.

3.2. Estimation of E^0 and k_{11} of $4\text{-BrC}_6\text{H}_4\text{CH}_2\text{CrL}(\text{H}_2\text{O})^{3+/2+}$

Only an irreversible oxidation wave at about 1.2 V was detected over the range from -0.10 to 1.40 V (with respect to a normal hydrogen electrode) up to a scan rate of 50 V s^{-1} , consistent with the expected instability of the $\text{RCrL}(\text{H}_2\text{O})^{3+}$ complex. Only single-exponential kinetic profiles were obtained in the reaction between $4\text{-BrC}_6\text{H}_4\text{CH}_2\text{CrL}(\text{H}_2\text{O})^{2+}$ and IrCl_6^{2-} under all the concentration conditions. The absence of a second stage, even with the highest IrCl_6^{2-} concentration applied (4.5×10^{-4} M), allows us to set a lower limit for k_3 , namely $k_3 > k_2 [\text{IrCl}_6^{2-}]_{\text{max}} = 60 \text{ s}^{-1}$. The same limit of k_3 , should hold for the oxidation by

ABTS^{•-} as well ($k_3' = k_3$). Since the ratio k_2/k_3 is already known ($6.7 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$) for ABTS^{•-}, we can set broad limits on k_{-2} , namely $4 \times 10^5 - 1 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which combined with $k_2 = 1.5 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $E^0 = 0.43 \text{ V}$ (for ABTS^{•-/2-}) affords an estimate for the reduction potential of 4-BrC₆H₄CH₂CrL(H₂O)^{3+/2+} of $0.89 \text{ V} > E^0 > 0.63 \text{ V}$. We therefore adopt the value $E^0 = 0.8 \pm 0.2 \text{ V}$.

Even though this value is rough, it is already much more concrete than the upper limit of 1.2 V based on the cyclic voltammogram. Generally speaking, using a kinetic method to determine thermodynamic properties such as E^0 demands more time than a direct electrochemical method such as cyclic voltammetry, but its effectiveness is unique in handling problems involving unstable reactive intermediates.

The Marcus [9] theory relates the driving force and SER constants k_{11} and k_{22} to the overall cross rate constants k_{12} :

$$2 \ln k_{12} = \ln k_{11} + \ln k_{22} + \frac{F}{RT} (E_{\text{ox}}^0 - E_{\text{red}}^0) \quad (10)$$

Substituting into eqn. (9) the known E_{ox}^0 and k_{22} values of IrCl₆^{2-/3-} (Table 1) and the E_{red}^0 value of BrC₆H₄CH₂CrL(H₂O)^{3+/2+} (0.8 V) together with the k_2' value (for k_{12}) measured in reactions (2'), we calculated the SER constant k_{11} of BrC₆H₄CH₂CrL(H₂O)^{3+/2+} couple to be $24 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Applying the same procedure to the reaction between an outer-sphere electron acceptor ABTS^{•-} and BrC₆H₄CH₂CrL(H₂O)²⁺ (so that an outer-sphere electron transfer process was assured), we calculated the k_{11} value to be $18 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Considering the error carried over

TABLE 1. Reduction potentials, self-exchange rate constants and cross-reaction rate constants^a pertaining to the oxidation of 4-BrC₆H₄CH₂CrL(H₂O)²⁺

Oxidant	k_{12} ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	k_{22} ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	E_{ox}^0 (V)
IrCl ₆ ²⁻	$(1.29 \pm 0.18) \times 10^4$	2.0×10^5 [13]	0.892 [8]
ABTS ^{•-}	$(1.51 \pm 0.17) \times 10^2$	2.2×10^9 (unpublished result)	0.43 [7]

^a At 25°C, $[\text{H}^+] = 1.0 \times 10^{-2} \text{ M}$, and $I = 2.0 \text{ M}$ maintained with sodium perchlorate.

from the estimate of $E^0 = 0.8 \text{ V}$ for the organochromium couple and the error added in by using the simplified Marcus equation, we believe that the two calculated k_{11} values are actually in good agreement with each other. This agreement is in accordance with the notion that chromium(III) complexes are substitutionally inert and usually react with oxidants via the outer-sphere electron transfer mechanism. We adopt the value $k_{11} = 2 \times 10 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. With the uncertainty in the E^0 value of the BrC₆H₄CH₂CrL(H₂O)^{3+/2+} couple, the SER constant may be better expressed as a range: $5 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} < k_{11} < 7 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Acknowledgments

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