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Kinetics of chain reactions between organochromium macrocyclic complexes and iodine

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Abstract

The organochromium complexes $RCrL(H_2O)^{2+}$ (R=2-Pr,2-Bu,$C_6H_5CH_2$, and 4-$MeC_6H_4CH_2$; L=[15]aneN$_4$) react with I_2. When $RCrL(H_2O)^{2+}$ is in excess, the reaction kinetics are dominated by a chain mechanism characterized by a rate law showing half-order dependence on I_2 concentration and one-and-a-half-order dependence on $RCrL(H_2O)^{2+}$ concentration. Rate constants for the chain reactions are (M^{-1} s^{-1}) $(1.75 \pm 0.07) \times 10^2$ for R=2-Pr, $(6.50 \pm 0.21) \times 10$ for R=2-Bu, $(4.51 \pm 0.17) \times 10$ for R=$C_6H_5CH_2$, and $(1.14 \pm 0.08) \times 10^3$ 4-$MeC_6H_4CH_2$. The effect of concurrent electrophilic substitution of $RCrL(H_2O)^{2+}$ by I_2 is small and varies with the structure of R. The reactivity trend of the family of $RCrL(H_2O)^{2+}$ (R includes 1°-alkyl, aralkyl, and 2°-alkyl) was discussed in terms of oxidation of $RCrL(H_2O)^{2+}$ and of steric hindrance around the α-carbon of R.

Keywords: Chromium; Kinetics; Chain reaction; Organochromium; Macrocytic

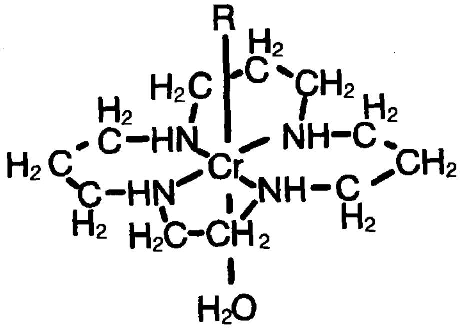
1. Introduction

Chain reactions have been observed with various inorganic [1] and organic molecules [2], but only a limited number of examples are known where cleavage of a transition metal–carbon bond of an organometallic compound is involved in the chain propagation process [3]. One such example is the chain reaction between 4-$BrC_6H_4CH_2CrL(H_2O)^{2+}$ (L=[15]aneN$_4$) and I_2 [4]. The present paper extends the kinetic and mechanistic study of the chain reaction of 4-$BrC_6H_4CH_2CrL(H_2O)^{2+}$ with I_2 to include two more aralkylchromium compounds $RCrL(H_2O)^{2+}$ (R=$C_6H_5CH_2$ and 4-$MeC_6H_4CH_2$) and two 2°-alkylchromium compounds (R=2-Pr and 2-Bu). Four 1°-alkylchromium compounds (R=Me, Et, Pr, Bu) were also included for the sake of comparison. The study described here aimed at establishing a more solid experimental foundation for the previously proposed chain mechanism (previously based only on one compound) and revealing the general reactivity trend of the whole family of $RCrL(H_2O)^{2+}$ compounds towards iodine.

2. Experimental section

2.1. Materials

All organochromium compounds $RCrL(H_2O)^{2+}$ with the following structure



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were synthesized according to the following reaction [5],

$$RX + CrL(H_2O)^{2+} \longrightarrow R\cdot + X^- + CrL(H_2O)^{3+} \quad (1)$$

$$R\cdot + CrL(H_2O)^{2+} \longrightarrow RCrL(H_2O)^{2+} \quad (2)$$

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from $CrL(H_2O)_2^{2+}$ and the corresponding organobromide RBr or organoiodide RI. The inorganic chromium macrocyclic complex, $CrL(H_2O)_2^{2+}$ was prepared by mixing equivalent amounts of $CrCl_2 \cdot 4H_2O$ and L (Strem Chemical Co.) in aqueous solution [6]. The organometallic dications, $RCrL(H_2O)^{2+}$, were isolated by ion exchange on Sephadex C-25. The following extinction coefficients (ϵ, M^{-1} cm^{-1}) were used to determine their concentrations: 3.28×10^3 at 287 nm and 5.50×10^2 at 396 nm for $2\text{-PrCrL}(H_2O)^{2+}$; 3.31×10^3 at 292 nm and 5.60×10^2 at 390 nm for $2\text{-BuCrL}(H_2O)^{2+}$; 7.92×10^3 at 273 nm, 7.47×10^3 at 297 nm and 2.17×10^3 at 353 nm for $C_6H_5CH_2CrL(H_2O)^{2+}$; 6.72×10^3 at 243 nm, 7.65×10^3 at 281 nm and 6.78×10^3 at 302 nm for $4\text{-MeC}_6H_4CH_2CrL(H_2O)^{2+}$; 3.30×10^3 at 258 nm and 2.27×10^2 at 375 nm for $MeCrL(H_2O)^{2+}$; 3.10×10^3 at 264 nm and 3.87×10^2 at 383 nm for $EtCrL(H_2O)^{2+}$; 3.44×10^3 at 265 nm and 4.65×10^2 at 383 nm for $1\text{-PrCrL}(H_2O)^{2+}$; 3.30×10^3 at 268 and 4.59×10^2 at 383 nm for $1\text{-BuCrL}(H_2O)^{2+}$ [5,7].

Iodine and sodium iodide solutions were prepared by dissolving corresponding AR-grade reagents in 0.01 M perchloric acid. Iron(II) perchlorate hexahydrate, $Fe(ClO_4)_2 \cdot 6H_2O$ was purchased from Aldrich and used without further purification.

2.2. Kinetics

The kinetics of the chain reaction between the organochromium complexes and iodine in aqueous solution at 25°C was studied with a Shimadzu UV-3103 PC UV-VIS-NIR scanning spectrophotometer. The reaction progress was monitored by following the disappearance of I_3^- at 352 nm [8]. Oxygen free conditions were maintained for all the measurements. In addition to the analysis of kinetic profiles and product distribution, the following control experiments were conducted to aid the assessment of the reaction mechanism: (1) variation of $[H^+]$ (pH 2 ~ 3); (2) variation of ambient light intensity; and (3) chain breakage where a small amount of Fe^{2+} or O_2 was introduced to intercept the chain process. In all cases, total ionic strength of the sample solutions was maintained at 0.20 M by using calculated amount of $NaClO_4$. Most of the kinetic data were collected under conditions where iodine was used as a limiting reagent (from 4.0×10^{-6} M to 2.1×10^{-5} M) and organochromium concentration was varied (from 3.4×10^{-5} M to 4.0×10^{-4} M).

2.3. Product analysis

Organic products RI and ROH (R=2-Pr and 2-Bu) were identified with a Shimadzu GC-14A gas chromatograph equipped with a 6 ft column packed with OV-101 stationary phase. The instrument was calibrated by use of standard organic halides and alcohols. Aralkyl iodides and alcohols ($R=C_6H_5CH_2$ and $4\text{-MeC}_6H_4CH_2$) were detected by an indirect spectroscopic method (vide infra). The inorganic products I_3^- and $CrL(H_2O)_2^{3+}$ were isolated by ion exchange on Sephadex C-25 and subsequently identified spectrophotometrically [5,7].

3. Results and discussion

3.1. Rate law

The reactions were studied at pH 2 (with two control experiments conducted at pH 3) under deaerated conditions with organochromium complexes in excess. All the organochromium compounds reacted with iodine under these conditions. No change in reactivity was detected over a pH change from 2 to 3. The reactions consumed iodine to produce iodide and cleaved the Cr–C bond in the organochromium compounds to generate an inorganic chromium complex and organic derivatives according to Eq. (3):

$$RCrL(H_2O)^{2+} + I_2 + H_2O \longrightarrow (RI + ROH) + CrL(H_2O)_2^{3+} + I^- \qquad (3)$$

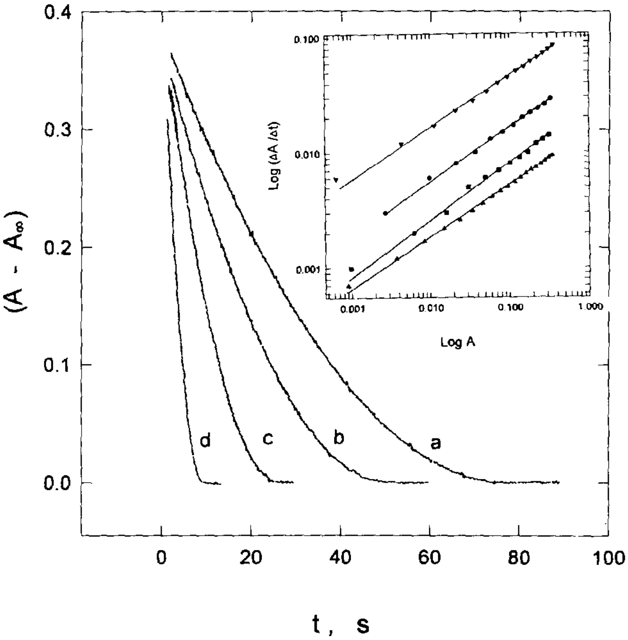

Fig. 1. Kinetic profiles of reactions between $RCrL(H_2O)^{2+}$ and I_2. (a) $R=C_6H_5CH_2$, $[RCrL(H_2O)^{2+}]_{av} = 1.83 \times 10^{-4}$ M, $[I_2]_{T,0} = 2.00 \times 10^{-5}$ M; (b) R=2-Bu, $[RCrL(H_2O)^{2+}]_{av} = 1.93 \times 10^{-4}$ M, $[I_2]_{T,0} = 1.94 \times 10^{-5}$ M; (c) R=2-Pr, $[RCrL(H_2O)^{2+}]_{av} = 1.58 \times 10^{-4}$ M, $[I_2]_{T,0} = 2.03 \times 10^{-5}$ M; (d) $R=4\text{-MeC}_6H_4CH_2$, $[RCrL(H_2O)^{2+}]_{av} = 9.06 \times 10^{-5}$ M, $[I_2]_{T,0} = 2.12 \times 10^{-5}$ M. Reaction temperature was 25°C. Monitored at 352 nm. Optical path length is 1 cm. $[I^-] = 5.00 \times 10^{-3}$ M. Inset: Linear correlation between $\log(\Delta A / \Delta t)$ and log A where absorbance A was measured at 352 nm and with an optical path length of 1 cm. $[I^-] = 5.00 \times 10^{-3}$ M. ▲: $R=C_6H_5CH_2$; ■: R=2-Bu; ●: R=2-Pr; ▼: $R=4\text{-MeC}_6H_4CH_2$.

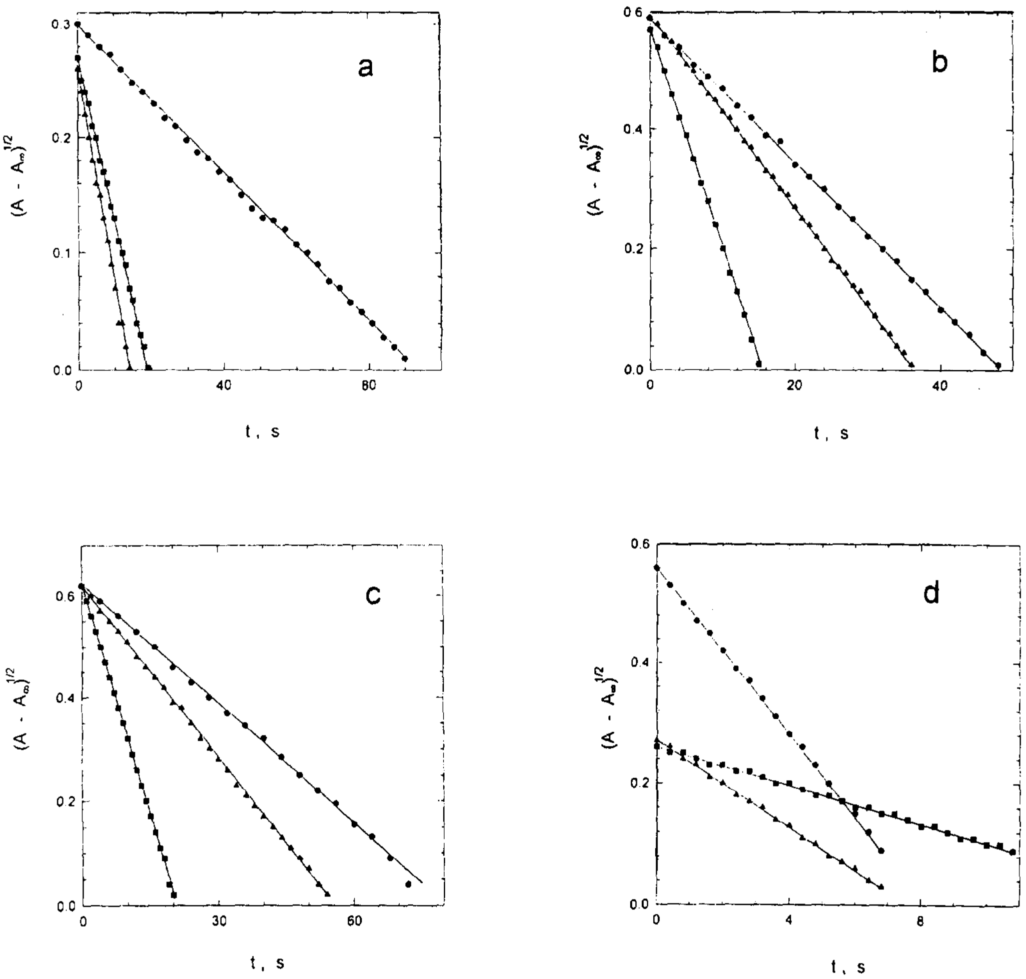

Fig. 2. Plots of $(A - A_\infty)^{1/2}$ vs. time. (a) R=2-Pr; (b) R=2-Bu; (c) R=$C_6H_5CH_2$; (d) R=4-$MeC_6H_4CH_2$.

For the reactions of aralkyl- and 2°-alkylchromium compounds with iodine, the kinetic profiles showed abrupt endings as depicted in Fig. 1, revealing typical characteristics of fractional order kinetics. Their empirical rate law was first derived roughly from double logarithmic plots of differential absorbance change with respect to time ($\Delta A/\Delta t$) versus varying absorbance (A), as shown in the inset of Fig. 1. The slopes obtained from these straight lines in the inset of Fig. 1 are between 0.46 and 0.52, indicating a pseudo-half-order rate law

$$\frac{dA}{dt} = -k_{obs}A^{1/2} \tag{4}$$

Eq. (4) can be expressed more explicitly in terms of reagent concentration

$$\frac{d[I_2]_T}{dt} = -k_{1/2}[I_2]_T^{1/2} \tag{5}$$

The composite rate constant $k_{1/2}$ can be related to the experimentally observed rate constant k_{obs} since $A = \epsilon l[I_3^-]$ and $[I_3^-] = K[I^-][I_2]_T/(K[I^-] + 1)$

$$k_{1/2} = \frac{k_{obs}(K[I^-] + 1)^{1/2}}{(\epsilon l K[I^-])^{1/2}} \tag{6}$$

where A and ϵ refer respectively to absorbance and extinction coefficients of I_3^- at 352 nm, $l = 1$ cm is the light path length used in this study, $K = 6.98 \times 10^2$

Table 1

Pseudo-half-order rate constants $k_{1/2}$ for the reaction of $RCrL(H_2O)^{2+}$ with I_2 [a]

$2\text{-PrCrL}(H_2O)^{2+}$		$2\text{-BuCrL}(H_2O)^{2+}$		$C_6H_6CH_2CrL(H_2O)^{2+}$		$4\text{-MeC}_6H_4CH_2CrL(H_2O)^{2+}$	
$[RCrL^{2+}]_{av}$, M	$k_{1/2}$, $M^{1/2}\ s^{-1}$	$[RCrL^{2+}]_{av}$, M	$k_{1/2}$, $M^{1/2}\ s^{-1}$	$[RCrL^{2+}]_{av}$, M	$k_{1/2}$, $M^{1/2}\ s^{-1}$	$[RCrL^{2+}]_{av}$, M	$k_{1/2}$, $M^{1/2}\ s^{-1}$
1.65×10^{-4}	3.48×10^{-4}	1.83×10^{-4}	1.74×10^{-4}	1.93×10^{-4}	1.12×10^{-4}	9.06×10^{-5}	9.82×10^{-4}
4.15×10^{-5}	4.68×10^{-5}	4.01×10^{-4}	5.36×10^{-4}	4.51×10^{-4}	4.32×10^{-4}	3.42×10^{-5}	2.28×10^{-4}
1.10×10^{-4}	2.02×10^{-4}	2.42×10^{-4}	2.33×10^{-4}	2.27×10^{-4}	1.64×10^{-4}	5.71×10^{-5}	5.15×10^{-4}
1.25×10^{-4}	2.65×10^{-4}	9.50×10^{-5}	6.02×10^{-5}	1.07×10^{-4}	4.99×10^{-5}		

[a] At 25°C; $[I^-] = 5.00 \times 10^{-3}$ M; pH = 2; ionic strength = 0.20 M.

M^{-1} [9] is the equilibrium constant of formation of I_3^- from I_2 and I^-, and $[I_2]_T$ stands for total iodine concentration, $[I_2]_T = [I_2] + [I_3^-]$.

The pseudo-half-order rate law (Eq. 4) was further confirmed by analyzing the absorbance change as a function of time in an integrated form. If reactions proceed as half-order processes, then Eq. (4) demands that $(A - A_\infty)^{1/2}$ decreases linearly with time. This was indeed observed experimentally. For every $RCrL(H_2O)^{2+}$ a family of straight lines was obtained when $(A - A_\infty)^{1/2}$ was plotted against time, Fig. 2, with their slopes ($= k_{obs}/2$) increasing with organochromium concentration. From Eq. (6), pseudo-half-order rate constants $k_{1/2}$ were calculated and they are listed in Table 1.

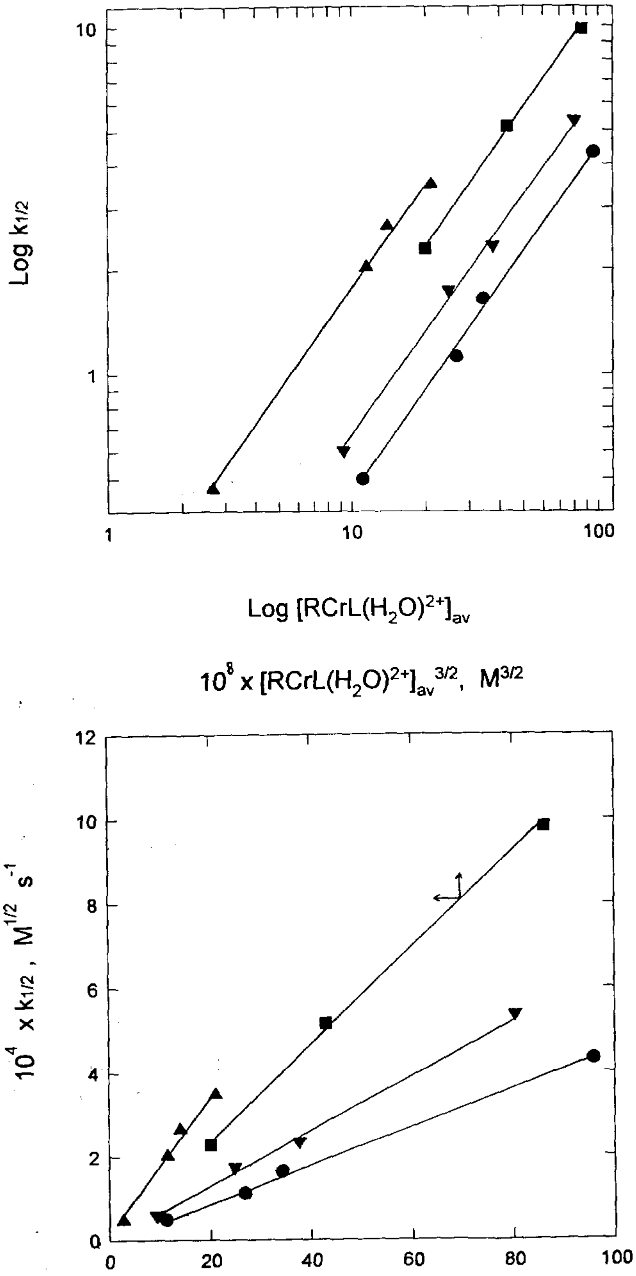

Fig. 3. (a) Linear correlation between log $k_{1/2}$ and log $[RCrL(H_2O)^{2+}]_{av}$ revealing slope of 1.5. ●: R=$C_6H_5CH_2$; ▼: R=2-Bu; ■: R=4-$MeC_6H_4CH_2$; ▲: R=2-Pr. (b) Plot of $k_{1/2}$ against $[RCrL(H_2O)^{2+}]_{av}^{3/2}$ with slopes correspond to k_{ch} values. ●: R=$C_6H_5CH_2$; ▼: R=2-Bu; ■: R=4-$MeC_6H_4CH_2$; ▲: R=2-Pr.

The explicit form of the dependence of $k_{1/2}$ on $[RCrL(H_2O)^{2+}]$ (R=aralkyl and 2°-alkyl) was revealed by plotting $\ln k_{1/2}$ against $\ln[RCrL(H_2O)^{2+}]$, as illustrated in Fig. 3(a). The common slope of ca 1.5 suggests an overall rate law of

$$\frac{d[I_2]}{dt} = -k_{ch}[I_2]^{1/2}\left[RCrL(H_2O)^{2+}\right]^{3/2} \qquad (7)$$

applicable to all of the four organochromium compounds. These kinetic data can be interpreted in terms of chain reactions between $RCrL(H_2O)^{2+}$ and I_2.

3.2. Chain mechanism

Electron transfer (Eq. (8)) is believed to be the common chain initiation step for all the four aralkyl- and 2°-alkylchromium compounds studied in this paper. Once the oxidized organochromium, $RCrL(H_2O)^{3+}$ is formed, it decomposes quickly via Cr–C bond homolysis to generate an aralkyl- or 2°-alkyl radical and an inorganic chromium(III) complex according to Eq. (9) of Scheme 1.

$$RCrL(H_2O)^{2+} + I_2 \longrightarrow RCrL(H_2O)^{3+} + I_2^- \qquad (8)$$

$$RCrL(H_2O)^{3+} \longrightarrow R\cdot + CrL(H_2O)^{3+} \qquad (9)$$

$$R\cdot + I_2 + I^- \longrightarrow RI + I_2^- \qquad (10)$$

$$R\cdot + I_2 + H_2O \longrightarrow ROH + H^+ + I_2^- \qquad (11)$$

$$RCrL(H_2O)^{2+} + I_2^- \longrightarrow RCrL(H_2O)^{3+} + 2I^- \qquad (12)$$

$$2I_2^- \longrightarrow I_3^- + I^- \qquad (13)$$

Scheme 1.

The carbon centred radical in turn passes the unpaired electron to I_2, one of the best radical scavengers ($\cdot Me + I_2 \rightarrow [\cdot MeI_2]$, $k = 6.0 \times 10^9$ M^{-1} s^{-1}, [10]) already existing in the solution, to generate the iodine anion I_2^-. Reaction 12 regenerates $RCrL(H_2O)^{3+}$ and completes the chain propagation cycle.

With $[\cdot R]$ and $[I_2^-]$ set at the levels of steady state concentration, the rate expression derived from Eqs. (8)–(13) has the form,

$$\frac{d[I_2]}{dt} = -k_{12}\frac{(k_8)^{1/2}}{(k_{13})^{1/2}}[I_2]^{1/2}\left[RCrL(H_2O)^{2+}\right]^{3/2} \qquad (14)$$

which agrees well with the experimental rate law of Eq. (7) and defines the empirical rate constant k_{ch} as

$$k_{ch} = k_{12}(k_8/k_{13})^{1/2} \tag{15}$$

Two pieces of key evidence supporting the chain propagation scheme of equations 9–12 have been accumulated since the first proposal of a similar scheme for the reaction between $4\text{-BrC}_6H_4CH_2CrL(H_2O)^{2+}$ and I_2 [4]. Firstly, it is proven that oxidative homolysis (reaction 9) occurred for every member of the $RCrL(H_2O)^{2+}$ family studied [7]. The oxidative homolysis rate constants ($> 10^2\ s^{-1}$) are about six orders of magnitude larger than the homolysis rate constants ($\sim 10^{-4}\ s^{-1}$) of $RCrL(H_2O)^{2+}$ [11], consistent with the fact that overall chain reaction rate (Eq. (14)) is independent of k_9. This is an important piece of information because reaction 9 (in conjunction with reaction 10 in Scheme 1) is responsible for the fast formation of RI. Direct homolysis of $RCrL(H_2O)^{2+}$

$$RCrL(H_2O)^{2+} \longrightarrow R\cdot + CrL(H_2O)^{2+} \tag{16}$$

and electrophilic attack of I_2 on $RCrL(H_2O)^{2+}$ are both too slow to account for the observed fast consumption of iodine and formation of RI. Secondly, experiments done under pulse radiolysis condition [12] showed that $RCrL(H_2O)^{2+}$ reacted with I_2^- (reaction 12) to generate $RCrL(H_2O)^{3+}$ and I^-. The corresponding rate constant is ca. $10^7\ M^{-1}\ s^{-1}$, varying somewhat with the R group. Qualitatively, this observation proves that Scheme 1 meets the long chain assumption. Quantitatively, the numerical value of $k_{12} \sim 10^7\ M^{-1}\ s^{-1}$ fits nicely in Eq. (15) (vide infra).

The fact that $RCrL(H_2O)^{2+}$ can be oxidized by a number of oxidants [13] ranging from mild ($ABTS^-$, E° $(ABTS^{-/2}) = 0.43$ V [14]) to strong ($IrCl_6^{2-}$, E° $(IrCl_6^{2-/3}) = 0.89$ V [15]) constitutes the basis for proposing Eq. (8). Based on the known reduction potential of $E°(I_2(aq)^{0/-1}) = 0.21$ V [16] and an estimate of $E°(RCrL(H_2O)^{2+}) = 0.8$ V for $R{=}BrC_6H_4CH_2$, [13], reaction 8 is anticipated to occur, but only to a small extent.

The reaction rates were discovered to be insensitive to the presence of room light in control experiments, hence photochemical processes are excluded from being responsible for the chain initiation process under the studied conditions. A close inspection of the rate law (Eq. (7)) also ruled out the possibility of attributing the chain initiation reaction to unimolecular Cr–C bond homolysis in the present case.

Two types of organic products, RI and ROH, were identified for either $2\text{-PrCrL}(H_2O)^{2+}$ or $2\text{-BuCrL}(H_2O)^{2+}$. Product RI was identified by an indirect spectroscopic test that consists of two stages. In the first stage, the reaction between I_2 and $2\text{-PrCrL}(H_2O)^{2+}$ or $2\text{-BuCrL}(H_2O)^{2+}$ was conducted with a slight excess of the latter. Then in the second stage a solution of $CrL(H_2O)^{2+}$ was added to react with any RI (R=2-Pr, 2-Bu) formed in the first stage. Upon this addition, corresponding $RCrL(H_2O)^{2+}$ was re-formed (via reactions 1 and 2) as confirmed by reappearance of its typical spectrum. After dilution factor was considered, the absorbance of newly formed $RCrL(H_2O)^{2+}$ in the second stage was used to evaluate concentrations of RI formed in the first stage. For both $2\text{-PrCrL}(H_2O)^{2+}$ and $2\text{-BuCrL}(H_2O)^{2+}$, about 95% of the $RCrL(H_2O)^{2+}$ used to react with I_2 in the first stage were recovered in the second stage. The missing 5% was converted to ROH (reaction 11) which does not react with $CrL(H_2O)^{2+}$ to regenerate $RCrL(H_2O)^{2+}$.

Quantitative evaluation of the RI : ROH ratio was further verified by GLC where both RI and ROH eluted and the amounts of RI and ROH were determined against pre-determined working curves (GLC peak area versus concentration) calibrated with standard RI and ROH at various concentrations. The results of the GLC experiments agreed well with those of the indirect spectroscopic experiments confirming that both RI and ROH were formed and the RI : ROH ratio is ca. 20 : 1. Low vapour pressure of the RI and ROH in the cases of $R{=}C_6H_5CH_2$ and $4\text{-MeC}_6H_4CH_2$ practically prevented these organic compounds from eluting out of the GLC column under the conditions we used, their RI : ROH ratios were determined by the above mentioned spectroscopic method. For $R{=}C_6H_5CH_2$, RI : ROH is ca. 30 : 1, and for $R{=}4\text{-MeC}_6H_4CH_2$, RI : ROH is ca. 10 : 1.

Under the conditions studied, the weak oxidant I_2 is only sufficient to oxidize $RCrL(H_2O)^{2+}$ to the extent to initiate a chain process (Eq. (8)) whereas a much stronger oxidant $I_2^-(E°(I_2^-/2I^-) = 1.13$ V [17]) is required to sustain the chain propagation (Eq. 11). With long chain approximation, the net result of coupled reactions 8–13 is reaction 3 which demands 1 : 1 stoichiometry between $RCrL(H_2O)^{2+}$ and I_2. This stoichiometric relation is confirmed experimentally by titration.

A technically important feature of Eq. (3) is that it converts iodine to iodide, which allows the strong light absorption of $I_3^-(I_3^- \rightleftarrows I_2 + I^-)$ at 352 nm ($\epsilon = 2.46 \times 10^4\ M^{-1}\ cm^{-1}$, [8]) to be used (with I^- added) to monitor the chain reaction with satisfactory precision. This is helpful because the light absorptions of all the other species are too weak within the wavelength range > 300 nm to permit any kinetic measurement of the reaction by spectrophotometric techniques. Between 200 and 300 nm, the overlaps among various charge transfer bands frustrated all attempts to collect meaningful kinetic data. In addition, care needs to be exercised to eliminate influence of a possible concurrent electrophilic substitution,

$$\mathrm{RCrL(H_2O)^{2+} + I_2 + H_2O \rightarrow RI + CrL(H_2O)_2^{3+} + I^-} \tag{17}$$

which should proceed according to a mixed second-order rate law [4]

$$\frac{d[\mathrm{I_2}]}{dt} = k_{\mathrm{el}}[\mathrm{I_2}]\left[\mathrm{RCrL(H_2O)^{2+}}\right] \tag{18}$$

In other words, organochromium complexes need to be used as excess reagents to take advantage of the formulas of $[\mathrm{I_2}]^{1/2}[\mathrm{RCrL(H_2O)^{2+}}]^{3/2}$ (for chain reaction) and $[\mathrm{I_2}][\mathrm{RCrL(H_2O)^{2+}}]$ (for electrophilic substitution). This requirement in turn makes it difficult to measure kinetic data by monitoring the change of organochromium concentration (a small change on a large background). Actually, the employment of $\mathrm{I_3^-}$ as chromophore has been critical to the success of the kinetic study of the chain reaction.

3.3. Chain carriers

Participation of $\mathrm{R\cdot}$ in the chain propagation process was diagnosed by the chain-breaking effect of $\mathrm{O_2}$. This technology was used previously for the reaction between $\mathrm{4\text{-}BrC_6H_4CH_2CrL(H_2O)^{2+}}$ and $\mathrm{I_2}$ [4]. Addition of $\mathrm{O_2}$ (~ 1 mM) caused not only retardation of the reaction but also changes of the appearance of the kinetic profiles with resulting kinetic traces resembling that of a pseudo-first-order reaction ($k'_{\mathrm{obs}}[\mathrm{I_2}]$). This effect is attributed to the well known radical scavenging capability of $\mathrm{O_2}$. Reaction

$$\mathrm{R\cdot + O_2 \rightarrow RO_2\cdot} \tag{19}$$

with $k_{19} = 4.9 \times 10^9$ $\mathrm{M^{-1}\ s^{-1}}$ is known [18].

The role of $\mathrm{I_2^-}$ as a chain carrier was confirmed by a similarly dramatic inhibition effect on reaction rate and on the appearance of kinetic profile observed when 0.5 mM of $\mathrm{Fe(ClO_4)_2(aq)}$ was added. The reaction

$$\mathrm{I_2^- + Fe^{2+} \rightarrow 2I^- + Fe^{3+}} \tag{20}$$

with $k_{20} = 3.6 \times 10^6$ $\mathrm{M^{-1}\ s^{-1}}$ [19] is believed to be responsible for the retardation of the reaction. No ROH was detected in the presence of $\mathrm{Fe^{2+}}$. This fact suggests that ROH was indeed derived from $\mathrm{R\cdot}$ in the chain process rather than from $\mathrm{RCrL(H_2O)^{2+}}$ via direct Cr–C bond decomposition. No reaction of $\mathrm{RCrL(H_2O)^{2+}}$ with $\mathrm{O_2}$ and $\mathrm{Fe^{2+}}$ was observed in blank experiments.

3.4. Reactivities of the organochromium compounds

At one extreme, no chain reaction with $\mathrm{I_2}$ was observed with 1°-alkylchromium compounds, $\mathrm{RCrL(H_2O)^{2+}}$ (R=Me, Et, Pr and Bu), even when $\mathrm{RCrL(H_2O)^{2+}}$ was used in large excess. The reaction between the 1°-alkylchromium compounds and iodine is always dominated by electrophilic substitution (Eq. 17). The empirical reaction order (as derived from the double-logarithmic plots) ranges between 0.9 and 1.1.

Table 2
Chain reaction rate constants k_{ch} and oxidation rate constants k_{ox} of $\mathrm{RCrL(H_2O)^{2+}}$

	k_{ch}, $\mathrm{M^{-1}\ s^{-1}}$	k_{ox}, $\mathrm{M^{-1}\ s^{-1}}$ [b]
$\mathrm{2\text{-}PrCrL(H_2O)^{2+}}$	1.75×10^2	8.54×10^4
$\mathrm{2\text{-}BuCrL(H_2O)^{2+}}$	6.50×10^1	4.87×10^4
$\mathrm{4\text{-}MeC_6H_4CH_2CrL(H_2O)^{2+}}$	1.14×10^3	4.60×10^5
$\mathrm{C_6H_5CH_2CrL(H_2O)^{2+}}$	4.51×10^1	3.86×10^4
$\mathrm{4\text{-}BrC_6H_4CH_2CrL(H_2O)^{2+}}$	1.83×10^1 [a]	1.29×10^4

[a] From Ref. [4]; [b] From Ref. [7].

At the other extreme, a nearly perfect fit of the observed kinetic data to the chain reaction mechanism (Fig. 2) was obtained with the aralkyl- and 2°-alkylchromium compounds. Numerical values of $\mathrm{k_{ch}}$ were calculated from the kinetic data in Fig. 3(b) using Eqs. (5) and (7) and are summarized in Table 2. From the nearly perfect fit of the kinetic data to the chain mechanism, one can conclude that electrophilic substitution is negligible.

For all the four aralkyl- and 2°-alkylchromium compounds studied in this paper, the electrophilic substitution by $\mathrm{I_2}$ had never been observed without interference of concurrent chain reaction even under extreme conditions like $[\mathrm{I_2}]_{\mathrm{T,0}} = 1.0$ mM and $[\mathrm{RCrL(H_2O)^{2+}}]_0 = 0.01$ mM. At this stage, we made no attempt to extract experimental information about their $\mathrm{k_{el}}$.

Between the two extremes, the reaction mechanism of $\mathrm{4\text{-}BrC_6H_4CH_2CrL(H_2O)^{2+}}$ with $\mathrm{I_2}$ varies with reagent concentrations [4]. Low organochromium and high iodine concentrations suppress the chain process and enhance the electrophilic substitution whereas high organochromium and low iodine concentrations allow the chain reaction to predominate.

Deviations of actual kinetic profile from an ideal linear relationship between $(A - A_\infty)^{1/2}$ and t were observed in the case of $\mathrm{C_6H_5CH_2CrL(H_2O)^{2+}}$ when $\mathrm{I_2}$ was used in excess ($[\mathrm{C_6H_5CH_2CrL(H_2O)^{2+}}] \sim 10^{-5}$ M and $[\mathrm{I_2}]_{\mathrm{T}} \sim 10^{-3}$ to 10^{-4} M). These kinetic data did not fit a first-order rate law either. Apparently, both the chain mechanism and the electrophilic substitution mechanism were operative under these conditions with neither predominant. A good fit of the observed kinetic data to first-order rate law (corresponding to predominant electrophilic substitution) was reported for the reaction between $\mathrm{4\text{-}BrC_6H_4CH_2CrL(H_2O)^{2+}}$ and $\mathrm{I_2}$ under similar concentration conditions [4].

No such deviation in the $(A - A_\infty)^{1/2}$ vs. t plots was observed for 2°-alkylchromium compounds even though the k_{ch} value of $\mathrm{2\text{-}BuCrL(H_2O)^{2+}}$ (6.50×10 $\mathrm{M^{-1}\ s^{-1}}$)

is comparable with that of $C_6H_5CH_2CrL(H_2O)^{2+}$ ($4.51 \times 10\ M^{-1}\ s^{-1}$). This is apparently attributable to the more severe steric hindrance around the 2°-carbon than that around the 1°-carbon. No such deviation was observed for $4\text{-}MeC_6H_4CH_2CrL(H_2O)^{2+}$ either, presumably because the k_{ch} value of this compound ($1.14 \times 10^3\ M^{-1}\ s^{-1}$) is much bigger than that of $C_6H_5CH_2CrL(H_2O)^{2+}$.

The general reactivity trend of the organochromium compounds, $RCrL(H_2O)^{2+}$, towards iodine can be summarized as follows

$$\begin{array}{ccc}\text{Importance of electrophilic substitution} & \underset{\longleftarrow}{\overset{\text{1°-RCr aralkyl 2°-RCr}}{\longrightarrow}} & \text{Importance of chain reaction}\end{array}$$

Within the family of aralkylchromium, reactivity towards chain reaction with I_2 increases in the order of $4\text{-}BrC_6H_4CH_2CrL(H_2O)^{2+} < C_6H_5CH_2CrL(H_2O)^{2+} < 4\text{-}MeC_6H_4CH_2CrL(H_2O)^{2+}$.

Three facts can be invoked to account for the observed difference in reactivity of the 1°-alkyl-, aralkyl- and 2°-alkylchromium complexes towards I_2. Firstly, the strong electron donating effect of the 2°-alkyl groups makes the 2°-alkylchromium complexes more susceptible to oxidation by I_2 (Eq. (8)) and I_2^- (Eq. (12)). Secondly, reaction 17 is disfavoured for the 2°-alkylchromium complexes as compared with their 1°-alkyl relatives for steric reasons. Thirdly, the 2°-alkyl and aralkyl radicals are more stable than the 1°-alkyl radicals. Therefore the homolysis reaction 9 is more energetically favoured for them. Apparently, the electronic donation capability of the R group and the stability of the $R\cdot$ radical are of utmost importance as demonstrated by the trend in reactivity within the family of aralkylchromium.

The k_{ch} values in Table 2 span nearly two orders of magnitude. A monotonic correlation can be seen between the k_{ch} values measured in this study and the published k_{ox} values for oxidation of $RCrL(H_2O)^{2+}$ by $IrCl_6^{2-}$ (also listed in Table 2). This correlation underlines the electron transfer character of the chain reactions between $RCrL(H_2O)^{2+}$ and I_2, which is consistent with Scheme 1 and the analytical formula of k_{ch} in Eq. (15). Taking k_{12} to be ca. $10^7\ M^{-1}\ s^{-1}$ [12], k_{13} to be ca. $10^9\ M^{-1}\ s^{-1}$ [20], and estimating k_8 to be ca. $10^{-1}\ M^{-1}\ s^{-1}$ by employing the Marcus equation [21], one can calculate k_{ch} from Eq. (15). The calculated value of k_{ch} is ca. $10^2\ M^{-1}\ s^{-1}$ which agrees qualitatively with experimentally measured values.

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[21] $k_8 = k_{ab} = (k_{aa}k_{bb}K_{ab})^{1/2}$ [22] with $k_{aa} \sim 10^9\ M^{-1}\ s^{-1}$ for $I_2^{0/1-}$ self-exchange reaction, $k_{bb} \sim 10^0\ M^{-1}\ s^{-1}$ for $RCrL(H_2O)^{3+/2+}$ self-exchange reaction [13], and $K_{ab} \sim 10^{-11}$ for the equilibrium constant of reaction 8, as estimated from $E°(I_2(aq)^{0/-1}) = 0.21$ V [16] and an estimate of $E°(4\text{-}BrC_6H_4CH_2CrL(H_2O)^{3+/2+}) = 0.8$ V [13].

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