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REACTION OF ORGANOCHROMIUM CATIONS WITH IODINE MONOBROMIDE

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Summary

Several members of the family of $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$ complexes have been shown to react cleanly with the interhalogen molecule IBr. Products of reaction are exclusively the organic iodide RI, $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, and Br^- ; RBr and $(\text{H}_2\text{O})_5\text{Cr}-\text{Br}^{2+}$ are not formed. Rates of the IBr reactions are comparable to those of bromine and much higher than those of iodine. These results are consistent with electrophilic reactions and suggest an S_E2 mechanism.

Introduction

Cleavage of the carbon-metal bond of organometallic compounds is a general reaction of halogens, a reaction of post-transition compounds such as organo-tin, -lead and -mercury compounds which has been widely studied [1-4]. Less attention has been paid to the reactions of organometallic derivatives of the transition metals, although kinetic determinations have been reported for reaction of $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$ with Br_2 and I_2 [5,6], as have stereochemical determinations for reaction of Br_2 with $\text{RMn}(\text{CO})_5$ (retention) [7], $\text{RFe}(\text{CO})_2-(\text{C}_5\text{H}_5)$ (inversion) [8], and $\text{RCo}(\text{dmgH})_2^*$ (inversion) [9,10]. The latter reaction has received considerable additional investigation, for in spite of the clean stereochemical result, other data suggest a mechanism more complicated than a single-step electrophilic cleavage [10-13].

In view of the complexities surrounding reaction of $\text{RCo}^{\text{III}}(\text{chel})$ with halogens, it appeared desirable to examine further reaction of $[(\text{H}_2\text{O})_5\text{Cr}^{\text{III}}-\text{R}]^{2+}$ cations, for which our earlier kinetic data had suggested a straightforward electrophilic reaction with halogen [5,6]. Toward this end we chose to examine the rate and products of reactions of certain key members of this family of complexes with the interhalogen IBr.

* *chel* = chelating tetradentate dianion; $(\text{dmgH})_2$ = bis(dimethylglyoximate).

Results and discussion

The reactions were studied in aqueous perchloric acid solutions in the absence of oxygen. (The benzyl- and isopropyl-chromium complexes are oxygen sensitive, especially the former [14], and we also wished to preclude in every case any reaction of O_2 with any intermediate species present.) Product determinations were carried out with excess CrR^{2+} at room temperature, and kinetic determinations at $25.0^\circ C$; in the latter cases ionic strength was controlled at $1.0 M$ by addition of lithium perchlorate. Extensive hydrolysis of IBr was avoided by preparing the IBr solutions in $1.0 M$ perchloric acid [15], and confirmed by the stability of the spectrum over a period of weeks. All of the solutions of IBr used for product studies, and many used for kinetic determinations, were made up to contain ca. 5–10% excess I_2 , thereby avoiding any trace of Br_2 from the original preparation or from the equilibrium $2IBr \rightleftharpoons I_2 + Br_2$. When this was not done, variable contamination from Br_2 reactions was found. The addition of the low level of I_2 was shown to be innocuous: not only is the rate of I_2 reaction >100 -fold lower than that of IBr, but variation of the low level of $[I_2]$ had no effect on the rate constants obtained.

The products of reaction

The only volatile product from reaction of $CrCH_2Cl^{2+}$ with IBr proved to be chloriodomethane ($>99\%$). This result was obtained by trapping the volatile products flushed from the reaction vessel with purified nitrogen in a U-tube cold trap. The sample was identified mass spectrometrically, agreeing with an authentic sample prepared by the method of Sakurai [16]: in particular CH_2ClBr was absent (the method would have revealed 0.3% of this product). Because this reaction was conducted in aqueous solution, whereas Dreos et al. [13] conducted the reaction of $RCo(chel)$ with ICl in chloroform, it was important to demonstrate that the result in the latter case of roughly equal yields of RCl and RI was not a solvent effect. For this reason the products of reaction of $[CH_3Co(salen)-H_2O]$ with IBr ($>2 : 1$ ratio) were determined by the same method. The mass spectral determinations gave a $1 : 1$ ratio of CH_3Br and CH_3I , the same result reported for reaction in chloroform.

The organic product from reaction of benzylchromium ion with IBr was determined to be benzyl iodide (exclusively; no RBr was detected, the confidence level is 90% owing to possible overlap with the solvent peak) using a gas chromatographic method calibrated with known samples of benzyl bromide and iodide.

The constitution of the chromium(III) product of reaction of $CrCH_2Cl^{2+}$ with IBr was examined after absorbing the products on a column of Dowex 50W-X8 cation exchange resin. Visual and spectrophotometric examination of the chromium(III) on the resin and after elution confirmed that it was $Cr(H_2O)_6^{3+}$, and no detectable amounts of $(H_2O)_5CrBr^{2+}$ or $(H_2O)_5CrI^{2+}$ were found. This result is identical with that for CrR^{2+} reactions with Br_2 [5], yet stands in contrast to the production of (depending upon reaction ratios) $Co^{II}(chel)$ and/or $XCo^{III}(chel)$ in the reactions of $RCo^{III}(chel)$ with halogens [13].

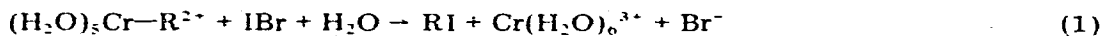
* $salen = N,N'$ -ethylenebis(salicylideneiminato).

TABLE 1
KINETIC DATA FOR $\text{Cr-R}^{2+} + \text{IBr}$ REACTIONS ^a

R	Range of reactant concentrations			Number of runs	$k(\text{IBr})$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)
	$10^4 \times [\text{IBr}] (\text{M})$	$10^4 \times [\text{Cr-R}^{2+}] (\text{M})$	$[\text{H}^+] (\text{M})$		
CH_2Cl	0.74–10.9	0.33–52.4	1.0	10	$6.3 \pm 0.6 \times 10^{-1}$
$\text{CH}(\text{CH}_3)_2$	8.3–15.8	0.74–1.1	1.0	4	$3.54 \pm 0.22 \times 10^1$
$\text{CH}_2\text{C}_6\text{H}_5$	3.75–8.35	0.35–0.71	0.5	4	$1.16 \pm 0.09 \times 10^6$
$\text{CH}_2\text{C}_6\text{H}_4\text{CH}_3$	3.46–4.69	0.38	0.5	2	$1.0 \pm 0.2 \times 10^6$
$\text{CH}_2\text{C}_6\text{H}_2\text{CF}_3$	3.46–5.21	0.38	0.5	5	$2.21 \pm 0.12 \times 10^5$

^a At 25.0° in aqueous solution with 1.0 M ionic strength.

Reaction of the organochromium(III) cations with aqueous iodine monobromide is thus established to occur according to the simple stoichiometry of reaction 1:



Kinetic determinations

We selected from a large number of known complexes a few members for quantitative kinetic studies, deciding not to conduct a study of a larger sample once we found a strong similarity between the IBr and Br_2 reactions. The CrR^{2+} complexes chosen include an alkyl [$\text{CH}(\text{CH}_3)_2$], a haloalkyl (CH_2Cl), and an aralkyl ($\text{CH}_2\text{C}_6\text{H}_5$), along with two derivatives of the latter.

The reaction rate was determined under conditions employing a pseudo-first-order excess of one reagent or the other, usually IBr, although in the reaction of $\text{CrCH}_2\text{Cl}^{2+}$ the chromium complex was in excess in several runs. In every case the pseudo-first-order rate plots were linear, and the rate constants so derived were directly proportional to the concentration of reagent in excess. These experiments confirm the same bimolecular rate expression for the IBr reaction (eq. 2) as found earlier for Br_2 and I_2 reactions [5,6]:

$$d[\text{RI}]/dt = k(\text{IBr})[\text{Cr-R}^{2+}][\text{IBr}] \quad (2)$$

Table 1 summarizes the kinetic data. Comparison with earlier results, where available [5,6], for $k(\text{Br}_2)$ and $k(\text{I}_2)$ establishes the reactivity pattern $k(\text{IBr}) \approx k(\text{Br}_2) \gg k(\text{I}_2)$. Production of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ rather than $\text{Cr}(\text{H}_2\text{O})_5\text{Br}^{2+}$ or $\text{Cr}(\text{H}_2\text{O})_5\text{I}^{2+}$ eliminates two additional mechanisms: (1) a four-centered S_{Ei} mechanism in which $\text{Cr-R}^{2+} + \text{X-Y}$ yields $\text{CrX}^{2+} + \text{RY}$ and (2) a process involving formation of Cr^{2+} , analogous to a known reaction of the cobalt complex (eq. 3), for not only are two organic halides not formed, but reoxidation of Cr^{2+} by halogen would necessarily produce a halo complex.



That the product of reaction of Cr-R^{2+} with IBr is RI rather than RBr provides further evidence for electrophilic reaction: the electropositive iodine

atom of IBr would be more electrophilic and have the greater tendency to react with the carbanion-like alkyl of $\text{Cr}^{\text{III}}-\text{R}^{2-}$. In this respect our results are like those found by Tauszer et al. [13] for the reaction of phenylcobalt complexes and bis(organo)cobalt complexes, in which instance only the organic iodide is produced. Presumably the reason is the same: these complexes are more "carbanion-like" in their reactivity, and thereby react preferentially by electrophilic mechanisms.

Experimental

The organochromium complexes were prepared and purified as reported in refs. 5 and 17. Iodine monobromide was prepared by halogen exchange [18] and recrystallized 2–4 times by slow cooling of the melt to just below its freezing point, decanting any remaining liquid. Solutions of IBr were prepared fresh as needed and were standardized by titration with sodium thiosulfate. Pure IBr solutions have λ_{max} 400 nm (ϵ 301 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) in 1.0 M perchloric acid.

Reaction rates were determined by the stopped-flow method using a Durrum instrument, except for the slower reaction of $\text{CrCH}_2\text{Cl}^{2-}$, for which a Cary Model 14 recording spectrophotometer with an expanded-scale slide wire was used. The GC determinations were performed using a HP-5711 analytical instrument with a 120 cm \times 0.3 cm column of SE-30 at 160°C and a flow of 1 cm³ per 2.5 s. Retention times were checked with authentic samples.

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