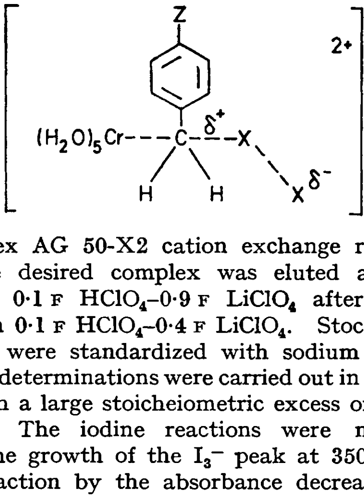
Substituent Effects in Electrophilic Cleavage Reactions of *para*-Substituted Benzylpenta-aquochromium Cations by Molecular Halogens

By JAMES C. CHANG and JAMES H. ESPENSON*

(*Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa* 50010)

Summary The kinetics of the reaction of p-Z-$C_6H_4CH_2Cr(OH_2)_5^{2+}$ with halogens in aqueous solution obey a second-order rate expression in which k_2 follows the Hammett equation for $Br_2(\rho = -1{\cdot}29)$ and $I_2(\rho = -0{\cdot}81)$.



(I)

CLEAVAGE reactions of organometallic compounds with halogens in solution have been widely studied,[1] but many of the reactions have been complicated by radical processes, trihalide ion reactions, and oxidation of the metal prior to metal–carbon bond cleavage. One series of compounds in which such complications appear to be absent is the reaction of an alkylpenta-aquochromium(III) cation with bromine in aqueous solution[2] [Equation (1)] To provide further

$$(H_2O)_5CrR^{2+} + Br_2 \rightarrow Cr(H_2O)_6^{3+} + RBr + Br^- \qquad (1)$$

information concerning dealkylation reactions with halogens, particularly the electronic effects in the transition state, kinetic studies of the reactions of substituted benzyl derivatives (Z being the *para* substituent) were carried out

$$p\text{-Z-}C_6H_4CH_2Cr(OH_2)_5^{2+} + X_2 \rightarrow Cr(H_2O)_6^{3+} + p\text{-}ZC_6H_4CH_2X + X^- \qquad (2)$$

for $X_2 = Br_2$ and I_2 in aqueous solution at 25·0 °C and 1·00 M ionic strength [Equation (2)]. The benzyl complexes were prepared with benzyl bromide and Cr^{II} and isolated under nitrogen by the method of Kochi and Davis,[3] using Dowex AG 50-X2 cation exchange resin, 50—100 mesh. The desired complex was eluted at 0° with a solution of 0·1 F $HClO_4$–0·9 F $LiClO_4$ after first eluting $CrBr^{2+}$ with 0·1 F $HClO_4$–0·4 F $LiClO_4$. Stock solutions of Br_2 and I_2 were standardized with sodium thiosulphate. The kinetic determinations were carried out in the absence of air and with a large stoicheiometric excess of the halogen, ⩾ 10 fold. The iodine reactions were monitored by following the growth of the I_3^- peak at 350 nm, and the bromine reaction by the absorbance decrease at 300 nm which is at or near a peak of each of the benzylchromium complexes. Pseudo-first-order rate plots were linear; k_{obs} showed a linear dependence upon $[I_2]$ or $[Br_2]$. The rate was independent of $[H^+]$ over the range 0·055—0·50 M. The kinetic data are consistent with equation (3). The

$$-d[Cr\text{-}CH_2C_6H_4Z^{2+}]/dt = k_X^Z\,[Cr\text{-}CH_2C_6H_4Z^{2+}][X_2] \qquad (3)$$

Table summarizes the rate constants and the Hammett substituent constants. The Cr^{III} product was shown to be $Cr(H_2O)_6^{3+}$, with <5% of the halogeno-complex $Cr(H_2O)_5X^{2+}$, affirming that a closed transition state is not involved.

TABLE

Rate constants[a] for the halogenation of p-Z-$C_6H_4CH_2Cr(H_2O)_5^{2+}$ at 25·0° and $\mu = 1.00$ M

Z	σ[b]	$k_I^Z \times 10^{-3}/M^{-1}\,s^{-1}$	$k_{Br}^Z \times 10^{-5}/M^{-1}\,s^{-1}$
CH_3	−0·17	4·76	—
H	0	4·20	8·3
Br	+0·23	2·26	2·32
CF_3	+0·54	1·39	1·55
CN	+0·66	1·06	0·96

[a] At $[H^+] = 0.50$ M except for Z = H with $X_2 = I_2$, where $[H^+]$ variation 0·055–0·50 M is included; [b] substituent constants from H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

Both reactions gave linear plots of log k_X^Z *vs.* σ_p, correlating well with the Hammett relation: equation (4) with

$$\log(k^Z/k^H) = \sigma_p\rho \qquad (4)$$

$\rho = -0.81$ for I_2 and -1.29 for Br_2. The negative values of ρ are consistent with the assigned S_E2 mechanism,[1b,1c,2,4] in which the halogen electrophile, with the positive end of an induced dipole, attacks the α-carbon atom. This suggests the transition state (I) where the charge symbols represent charge separations relative to those in the ground state. The benzyl carbon centre is less negative in the transition state than in the ground state, consistent with the S_E2 mechanism. The negative value of ρ also indicates that the predominant rate process is C–X bond making and not Cr–C or X–X bond breaking. The slightly more negative value of ρ for bromine compared with iodine is consistent with the necessary polarization of the halogen molecule considering its greater electronegativity.

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[4] M. H. Abraham in "Comprehensive Chemical Kinetics", vol. 12, ed. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1973, pp. 215—218.