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Kinetics and Mechanisms of the Reactions of the 17-Electron Metal-Centered Radical $CpCr(CO)_3^•$ with Organic Halides

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Summary: An investigation of the kinetics of the reactions of $[CpCr(CO)_3]_2$ *with alkyl halides RX (RX =* $BrCH_2CO_2CH_3$, CF_3CH_2I, $BrCH_2CN$, $p\text{-}NO_2C_6H_4CH_2Br$*), which give the compounds* $CpCr(CO)_3X$ *and* $CpCr(CO)_3R$*, suggests that the reactions involve direct halogen abstraction from RX by the metal-centered radical* $CpCr(CO)_3$*, which is in equilibrium with the dimer.*

A very important class of reactions of metal-centered radicals, $ML_n^•$ (M = metal, L_n = ligands), is that in which the radicals take part in atom abstraction reactions. In the case of reactions with various organic halides, RX, the halogen atom X is commonly abstracted by $ML_n^•$ to form the halo complexes ML_nX and the carbon-centered radical $R^•$; the latter can then participate in a variety of secondary processes leading to exceedingly useful organic transformations (M = Sn, Fe, Co).[1] Details of the mechanisms by which halogen (and other) atom abstraction reactions proceed are thus of fundamental importance, and in recent years numerous investigations of the reactions of metal-centered radicals with alkyl halides have been carried out.[2] However, in many cases, metal-centered radicals have been generated via photolysis of the corresponding metal–metal-bonded dimers (eq 1). In most such cases, the steady-state concentrations of the organic and metal-centered radicals generated were too low for secondary processes such as coupling of metal- and carbon-centered radicals to be observed, and the fates of the resulting organic radicals could not be determined. In only a few cases, where the metal-centered radicals are stable with respect to dimerization, has coupling been observed to yield isolable amounts of the alkyl complexes ML_nR.[3] The stoichiometries of such reaction sequences are as in eq 2.

$$[ML_n]_2 \rightarrow 2ML_n^• \tag{1}$$

$$2ML_n^• + RX \rightarrow ML_nX + ML_nR \tag{2}$$

$$ML_n^• = \{CpCr(CO)_3\},^{3a-c} \{Rh(dmgH)_2PPh_3\},^{3d} \{[Co(CN)_5]^{3-}\},^{3e} \{Co(dmgH)_2PPh_3\}^{3f}$$

Two mechanisms have been considered for these reactions, involving either initial halogen atom abstraction followed by coupling of metal- and carbon-centered radicals (eqs 3 and 4) or initial electron transfer followed by halide ion

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[⊗] Abstract published in *Advance ACS Abstracts*, November 1, 1993.

[1] (a) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon Press: Oxford, U.K., 1986. (b) Curran, D. P. *Synthesis* **1988**, 417, 489. (c) Jasperse, C. P.; Curran, D. P.; Fevig, T. L. *Chem. Rev.* **1991**, *91*, 1237. (d) Giese, B.; Thoma, G. *Helv. Chim. Acta* **1991**, *74*, 1135.

[2] For an excellent overview, see: Brown, T. L. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: Amsterdam, 1990; p 67. (b) See also: Choi, M.-G.; Brown, T. L. *Inorg. Chim. Acta* **1992**, *198–200*, 823.

[3] (a) Cooley, N. A.; Watson, K. A.; Fortier, S.; Baird, M. C. *Organometallics* **1986**, *5*, 2563. (b) Goulin, C. A.; Huber, T. A.; Nelson, J. M.; Macartney, D. H.; Baird, M. C. *J. Chem. Soc., Chem. Commun.* **1991**, 798. (c) MacConnachie, C. A.; Nelson, J. M.; Baird, M. C. *Organometallics* **1992**, *11*, 2521. (d) Howes, K. R.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1988**, *27*, 3147. (e) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1969**, *91*, 582. (f) Halpern, J.; Phelan, P. F. *J. Am. Chem. Soc.* **1972**, *94*, 1881.

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transfer (eqs 5 and 6).

$$\mathrm{ML}_n^{\bullet} + \mathrm{RX} \rightarrow \mathrm{ML}_n\mathrm{X} + \mathrm{R}^{\bullet} \qquad (3)$$

$$\mathrm{ML}_n^{\bullet} + \mathrm{R}^{\bullet} \rightarrow \mathrm{ML}_n\mathrm{R} \qquad (4)$$

$$\mathrm{ML}_n^{\bullet} + \mathrm{RX} \rightarrow \mathrm{ML}_n^{+} + \mathrm{RX}^{-} \qquad (5)$$

$$\mathrm{ML}_n^{+} + \mathrm{RX}^{-} \rightarrow \mathrm{ML}_n\mathrm{X} + \mathrm{R}^{\bullet} \qquad (6)$$

In cases where, for instance, the rates of reaction exhibit a dependence on the carbon–halogen bond strength, it is believed that halogen atom transfer is the rate-determining step. In some cases, however, a better correlation appears to exist between the rates of reaction and the reduction potentials of the organic halides, and electron-transfer processes may well apply.[2]

We have previously reported that the chromium-centered radical $CpCr(CO)_3$, which exists in solution in equilibrium with the dimer $[CpCr(CO)_3]_2$ (eq 7)[4]

$$[\mathrm{CpCr(CO)_3}]_2 \rightleftarrows 2\mathrm{CpCr(CO)_3} \qquad (7)$$

reacts in toluene with many organic halides as in eq 8.[3a–c]

$$[\mathrm{CpCr(CO)_3}]_2 + \mathrm{RX} \rightarrow \mathrm{CpCr(CO)_3X} + \mathrm{CpCr(CO)_3R} \qquad (8)$$

$$\mathrm{R} = \mathrm{CH_3,\ CH_2CH{=}CH_2,\ CH_2CH{=}CHCO_2CH_3,\ CH_2C_6H_5,\ CH_2CO_2R'\ (R' = Me, Et),\ CH_2CN,\ CH(CO_2Me)_2;\ X = Br, I}$$

As the rates of the reactions correlated qualitatively with decreasing R–X bond strengths, it was suggested that the reactions involve rate-determining transfer of halogen atoms followed by rapid coupling of the organic radicals, as in eqs 3 and 4. Since the chromium dimer provides a rare example of an organometallic system in which sufficiently high steady-state concentrations of metal-centered radicals are achieved that their reactions with the alkyl radicals may be studied, the system is of unusual interest and we are carrying out a kinetics study of the reactions of $[CpCr(CO)_3]_2$ with a series of alkyl halides. We present here the results of our preliminary findings.

Our initial investigations have been carried out by utilizing four non-β-hydrogen-containing organic halides, $BrCH_2CO_2CH_3$, CF_3CH_2I, $BrCH_2CN$, and p-NO_2-$C_6H_4CH_2Br$, chosen because their reactions proceed cleanly as in eq 2 and can be conveniently monitored by ^{1}H NMR spectroscopy over a temperature range of at least 20 K. In all cases, the kinetics studies have been carried out under pseudo-first-order conditions in toluene-d_8, the organic halide concentrations being 0.026–1.3 M and total chromium concentrations being 0.002–0.03 M.

The presence of exchange processes between the halochromium products and the chromium radical/dimer[3c] precludes monitoring the reactions by either observation of the appearance of the Cp resonances of $CpCr(CO)_3X$ or the disappearance of the broad resonance of the dimer–monomer. However, as the products $CpCr(CO)_3X$ and $CpCr(CO)_3R$ are formed in 1:1 ratios, the reactions may be monitored by observation of the formation of the alkyl products $CpCr(CO)_3R$, which do not engage in exchange processes.[3c,5]

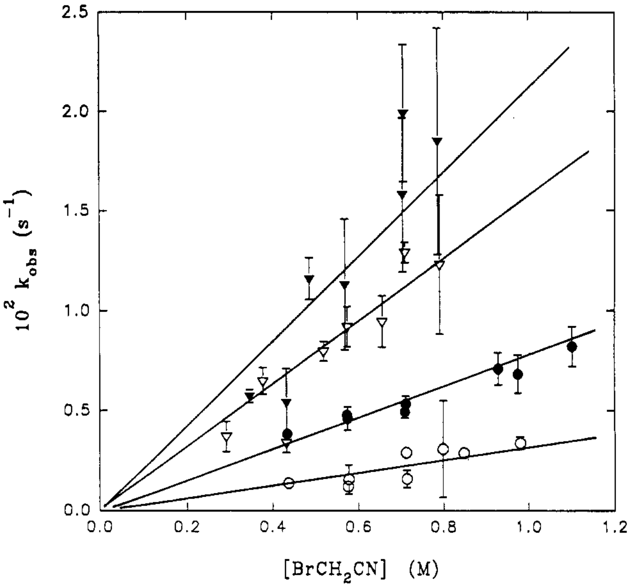

Figure 1. Plots of the first-order dependence of k_{obs} on $[BrCH_2CN]$ at 246 (○), 252 (●), 257 (▽), and 263 K (▼). The slopes of the solid lines represent twice the second-order rate constants reported in Table I.

The kinetics data were analyzed utilizing an integrated rate expression (eq 9), derived in the supplementary material. Equation 9 resembles that derived previously

$$\frac{(8K_{eq}([\mathrm{Cr}]_0 - 2[\mathrm{CrR}]) + K_{eq}^{\,2})^{1/2} - K_{eq}}{K_{eq}} + \ln((8K_{eq}[[\mathrm{Cr}]_0 - 2[\mathrm{CrR}]] + K_{eq}^{\,2})^{1/2} - K_{eq}) = -2k[\mathrm{RX}]t + \text{constant} \qquad (9)$$

for substitution reactions of $[CpCr(CO)_3]_2$ with tertiary phosphines;[6] it takes into account the preequilibrium of eq 7 and assumes that the reaction described by eq 4 is irreversible.

The values of K_{eq} were calculated from an average of the thermodynamic parameters reported by McLain[4a] (ΔH = 15.8 ± 0.4 kcal mol^{-1}, ΔS = 37.1 ± 1.4 cal K^{-1} mol^{-1}) and Watkins *et al.*[4b] (ΔH = 14.7 ± 0.3 kcal mol^{-1}, ΔS = 35.1 ± 0.9 cal K^{-1} mol^{-1}). The observed rate constants, k_{obs} ($=2k[RX]$), were determined from the slopes of the plots of the left side of eq 9 against time; the plots were linear for 1–5 half-lives, depending on reaction conditions.[7] Plots of k_{obs} against [RX] (Figure 1) indicate first-order relationships, with intercepts of zero within experimental uncertainty. The second-order rate constants k reported

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[4] (a) McLain, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 643. (b) Watkins, W. C.; Jaeger, T.; Kidd, C. E.; Fortier, S.; Baird, M. C.; Kiss, G.; Roper, G. C.; Hoff, C. D. *J. Am. Chem. Soc.* **1992**, *114*, 907.

[5] We have confirmed that the 1:1 product stoichiometry pertains in the case of the kinetics study involving $BrCH_2CO_2CH_3$. By periodic cooling of the reaction mixture to 240 K, at which temperature the individual Cp resonances of $[CpCr(CO)_3]_2$, $CpCr(CO)_3Br$, and $CpCr(CO)_3R$ could be observed, the mass balance of the reaction could be monitored directly.

[6] Watkins, W. C.; Hensel, K.; Fortier, S.; Macartney, D. H.; Baird, M. C.; McLain, S. J. *Organometallics* **1992**, *11*, 2148. In eq 9, $[Cr]_0$ is the initial chromium concentration on a chromium atom basis, [CrR] is the concentration of alkylchromium compound, $CpCr(CO)_3R$, at time t, and the constant is given by

$$\text{constant} = \frac{(K_{eq}^{\,2} + 8[\mathrm{Cr}]_0K_{eq})^{1/2} - K_{eq}}{K_{eq}} + \ln((K_{eq}^{\,2} + 8[\mathrm{Cr}]_0K_{eq})^{1/2} - K_{eq})$$

[7] Reactions involving higher concentrations of reactants or run at higher temperatures exhibited broadened resonances, thus making spectral integrations less accurate.

Table I. Second-Order Rate Constants for the Reactions of $CpCr(CO)_3$ with Alkyl Halides

RX	T (K) (±1)	10^3k (M^{-1} s^{-1})
$BrCH_2CO_2CH_3$	274	0.171 (±0.022)
	280	0.352 (±0.060)
	285	0.675 (±0.180)
	291	1.26 (±0.22)
	296	1.77 (±0.34)
CF_3CH_2I	274	0.403 (±0.114)
	280	0.875 (±0.165)
	285	1.34 (±0.16)
	291	3.59 (±0.88)
$BrCH_2CN$	246	1.56 (±0.36)
	252	3.86 (±0.32)
	257	7.80 (±0.90)
	263	10.5 (±2.6)
p-$NO_2C_6H_4CH_2Br$	263	22.0 (±4.1)
	269	27.5 (±5.6)
	274	64.5 (±20)
	280	108 (±25)

Table II. Activation Parameters

RX	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal K^{-1} mol^{-1})
$BrCH_2CO_2CH_3$	16.8 (±1.8)	−19 (±6)
CF_3CH_2I	19.5 (±2.6)	−8 (±8)
$BrCH_2CN$	13.8 (±2.1)	−19 (±6)
p-$NO_2C_6H_4CH_2Br$	14.1 (±3.4)	−11 (±10)

in Table I are an average of the values determined from $k_{obs}/2[RX]$ at each of four or five temperatures, from which the corresponding activation parameters, presented in Table II, were calculated.

That the reactions do indeed proceed as in eqs 3 and 4, with the halogen atom abstraction being dominant in the rate-determining step, is suggested by the observation of second-order rate laws, as well as by observations that the reactions of ICH_2CN and ICH_2CO_2Et proceed too rapidly (>20 M^{-1} s^{-1}), even under second-order conditions at 230 K, to be monitored satisfactorily. A transition state involving interaction of a halogen lone pair with the singly occupied molecular orbital (SOMO) of $CpCr(CO)_3$ seems likely, as has been proposed for CO substitution reactions of this metal-centered radical.[6] However, we note that the carbon–iodine bond strength of CF_3CH_2I[8a] is 56.3 kcal mol^{-1}, while the carbon–bromine bond strength of p-$NO_2C_6H_4CH_2Br$ is presumably similar to that of benzyl bromide[8b] (54.7 kcal mol^{-1}). These carbon–halogen bonds are therefore stronger than the carbon–iodine bonds of n-alkyl iodides,[8b] which react very slowly with $[CpCr(CO)_3]_2$,[3c] and partial electron transfer in the transition states for reactions of the more electrophilic organic halides seems possible.[9] However, although accurate estimates of the rate constants for reactions of $[CpCr(CO)_3]_2$ with benzyl bromide and p-methylbenzyl bromide cannot be obtained using the NMR procedures utilized above,[10] we find that the reactivities of benzylic bromides in toluene-d_8 decrease in the order p-NO_2 ≥ p-Me > p-H and that the rate of reaction of benzyl bromide varies little on going from toluene to the more polar tetrahydrofuran. Thus, the outer-sphere electron-transfer process of eqs 5 and 6 is presumably not a *significant* factor in these reactions. Largely on the basis of analogous substituent effects, a degree of electron transfer has also been postulated for halogen abstraction reactions from organic halides by several other metal-centered radicals.[2b,3d,f,11]

The rate constants for halogen abstraction by $CpCr(CO)_3$ are much smaller than those reported for several other 17-electron compounds,[2b,3d,f,11] consistent with the fact that $CpCr(CO)_3$ is a relatively stable radical, i.e. stable with respect to dimerization.[3a–c] Little may be said about the activation enthalpy data of Table II, but the entropies of activation are much as might be expected for an associated process.[12] There are surprisingly few data in the literature with which to make comparisons, but entropies of activation for bromine abstraction reactions of (dimethylglyoximato)cobalt(II) complexes with benzyl bromide are more strongly negative,[3f] while entropies of activation for self-exchange reactions of the $CpM(CO)_3^-/CpM(CO)_3X$ (M = Mo, W) halide couples are highly variable.[13]

Our research continues on extensions to the above work, and with alkyl halides containing β-hydrogen atoms, which take part in considerably more complex sequences of reactions.[3b,c]

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Supplementary Material Available: Text giving the derivation of the rate law used (4 pages). Ordering information is given on any current masthead page.

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(9) We note that α-ester, α-trifluoromethyl, and α-cyano groups seem generally to activate organic halides to halogen abstraction processes by radicals, thus rationalizing the reactivities of CF_3CH_2I, $BrCH_2CO_2CH_3$, and $BrCH_2CN$. See, for instance: (a) Danen, W. C.; Winter, R. L. *J. Am. Chem. Soc.* **1971**, *93*, 716. (b) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151.

(10) The methylene resonances of $C_6H_5CH_2Br$ and p-$MeC_6H_4CH_2Br$ overlap the methyl resonance of toluene.

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(13) Schwartz, C. L.; Bullock, R. M.; Creutz, C. *J. Am. Chem. Soc.* **1991**, *113*, 1225.