

OCTAHEDRAL METAL CARBONYLS

XXXIII*. KINETICS AND MECHANISM OF REACTIONS OF THE GROUP VIB METAL CARBONYLS WITH TETRABUTYLAMMONIUM HALIDES

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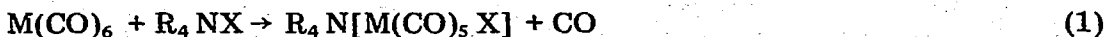
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Summary

The Group VIB metal carbonyls, $M(\text{CO})_6$ ($M = \text{Cr}, \text{Mo}, \text{W}$) react with tetra-butylammonium halides ($X = \text{Cl}, \text{Br}, \text{I}$) in chlorobenzene to afford the $\text{Bu}_4\text{N}-[\text{M}(\text{CO})_5\text{X}]$ products. For $M = \text{Mo}$ and W , the reactions obey a rate law, $-\text{d}[\text{M}(\text{CO})_6]/\text{dt} = k_2 \cdot [\text{M}(\text{CO})_6] \cdot [\text{Bu}_4\text{X}]$, while for $M = \text{Cr}$, an additional halide-independent term, ascribable to rate-determining dissociation of CO from the substrate, also is observed. The observed variations in rate as a function of the identity of the metal atom and the halide suggest that the second-order path involves attack of the halide at the metal atom for Mo and W, but at a carbonyl carbon for Cr. Rates of reaction increase in the order $\text{I} < \text{Br} < \text{Cl}$, consistent with an important influence of the steric nature of the halide upon the rate.

Introduction

The reaction of the Group VIB metal carbonyls with halides, usually as the tetraalkylammonium or *N*-methylpyridinium salts, afford the $\text{M}(\text{CO})_5\text{X}^-$ anions [2–4].



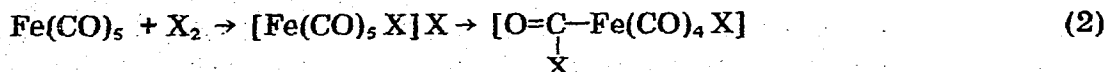
Analogously, $\text{XMn}(\text{CO})_5$ reacts with X^- to afford the *cis*- $[\text{Mn}(\text{CO})_4\text{X}_2]^-$ products, a process which a kinetic investigation indicated to proceed via rate-determining dissociation of CO from the substrate [5]. However, the conditions under which reactions of $\text{M}(\text{CO})_6$ with tetraalkylammonium halides proceed [over sixteen hours in refluxing 1,2-dimethoxyethane (glyme) b.p. 85.2° [6]]

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are far too mild for this mechanism to be applicable. Extrapolation of an Arrhenius plot of first order rate data for reaction of $W(CO)_6$ with tributylphosphine [7] would indicate the reaction of halides with that substrate in glyme via a first order process to be less than 1% complete over 16 h.

Moreover, it is known that the azide ion, a pseudo-halide, reacts with the Group VIB metal carbonyls by way of a rate law which is first order in azide concentration. The identity of the reaction products, $[M(CO)_5 NCO]^-$, strongly supports initial attack by the azide ion at a carbonyl carbon, followed by a subsequent Curtius-type degradation, to afford the isocyanate products [8]. Also of interest in this regard is the proposal of Noack of haloacyl intermediates to the reaction of iron pentacarbonyl with halogens in 2/3 chloroform/dichloromethane mixtures at -30° [9], (eqn. 2).



This conclusion was based upon the appearance of carbonyl stretching absorptions in the $1600-1700\text{ cm}^{-1}$ region of the infrared during the course of the reaction.

Our interest in the kinetics and mechanism of the latter reaction [10], and of reactions of metal carbonyls in general, has prompted a kinetic study of the reactions of the Group VIB metal carbonyls with halides, the results of which are reported here.

Experimental

Materials

The tetrabutylammonium halides ($X = Cl, Br, I$) were obtained from Eastman Organic Chemicals (Eastman Kodak Company), and were twice recrystallized from chlorobenzene. The chloride salt retained solvent of crystallization, which was removed by heating at 100° under high vacuum (0.05 mm) for four hours. The hexacarbonyls were obtained from Pressure Chemical Company [$Cr(CO)_6$ and $W(CO)_6$] and Climax Molybdenum Company [$Mo(CO)_6$] and were purified through sublimation under high vacuum at or near room temperature. Chlorobenzene was twice distilled from P_2O_5 onto molecular sieves.

Determination of reaction rates

Reaction rates were determined employing a Perkin-Elmer Model 621 grating spectrophotometer under pseudo-first-order reaction conditions (at least a 12-fold excess of the halide) through observation of the decrease in intensity of the T_{1u} carbonyl stretching mode of the substrate (ca. 1985 cm^{-1}). Solutions were ca. $1 \times 10^{-3}\text{ M}$ in hexacarbonyl. Sampling techniques have been described previously [11]. For the faster reactions, samples were withdrawn from the reaction vessel, were injected into evacuated test tubes sealed with rubber septa, and were stored at room temperature for later determinations of substrate absorbance. The reactions for $Cr(CO)_6$ were monitored employing gas-tight syringes (Hamilton) as reaction vessels [7] to eliminate the gas phase and thus prevent sublimation of the substrate during the course of the reaction. Several

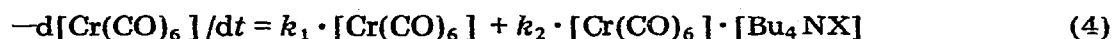
runs at 120.0° and low $[\text{Cr}(\text{CO})_6]$ employing the conventional reaction vessel demonstrated that evolved CO trapped in the gas-tight syringe did not affect the rate of reaction. The reaction products were found not to absorb significantly at the wavelength monitored, and thus the absorbance of a solvent-halide blank (A_{blank}) was employed in lieu of an A_{∞} value. Plots of $\ln(A_t - A_{\text{blank}})$ vs. t were generally linear to 1.5-3 half-lives depending upon the system studied and the concentration of the halide employed. All data were treated employing a linear least-squares computer program; the cited limits of error (in parentheses) are one standard deviation.

Identification of reaction products

The six combinations of substrate and halide investigated kinetically were allowed to react in chlorobenzene under conditions which approximated closely those employed in the kinetic runs. The carbonyl stretching spectra of the solutions at t_{∞} were compared to those reported previously (as KBr pellets or, for the iodides, in CHCl_3) [4]. The comparisons confirmed the $\text{Bu}_4\text{N}[\text{M}(\text{CO})_5\text{X}]$ species to be the sole reaction products.

Results and discussion

Rate (k_{obs}) data are exhibited in Table 1. Plots of k_{obs} vs. $[\text{Bu}_4\text{NBr}]$ for its reaction with $\text{W}(\text{CO})_6$ at three temperatures are shown in Fig. 1. First- and second-order rate constants, and activation parameters, where applicable, are given in Table 2. The results for reaction of $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ support the rate law given in eqn. 3, while for $\text{Cr}(\text{CO})_6$ a two-term rate law (eqn. 4)



is observed. The first-order term in eqn. 4 may reasonably be attributed to rate-determining dissociation of CO to form a $\text{Cr}(\text{CO})_5$ activated complex or intermediate, followed by its subsequent rapid attack by the halide to afford the observed products. A similar mechanism has been proposed for the ligand-independent path observed for reaction of $\text{Cr}(\text{CO})_6$ with Lewis bases, e.g., tributylphosphine, in decalin [7]. The first-order rates observed in the present study are some 50% higher than the corresponding values for reaction of $\text{Cr}(\text{CO})_6$ with Lewis bases, as determined through extrapolation of the Arrhenius plot of data at three temperatures for the latter reaction. It is reasonable to expect larger first-order rate constants in chlorobenzene than in decalin, since the greater polarity of chlorobenzene can produce a greater solvent interaction in the transition state, lowering the activation energy. Thus, for example, a similar increase in rate of unimolecular dissociation of CO has been noted for reaction of $\text{Ni}(\text{CO})_4$ with triphenylphosphine in chlorobenzene, as compared to n-heptane [12].

A halide-dependent path is observed for each of the three metal carbonyls with each halide. This observation may be contrasted to results for reaction of $\text{Mn}(\text{CO})_5\text{X}$ with X^- , for which the strongly-labilizing halide substituent makes

TABLE 1

RATES OF REACTION OF METAL HEXACARBONYLS WITH TETRABUTYLAMMONIUM HALIDES IN CHLOROBENZENE AT VARIOUS TEMPERATURES

Metal (Halide) T (°C)	[X ⁻] (M)	10 ⁴ × k _{obs} (sec ⁻¹)	Metal (Halide) T (°C)	[X ⁻] (M)	10 ⁴ × k _{obs} (sec ⁻¹)
Cr(Br) 120.0	0.0300	1.30(5)	W(Br) 100.0	0.0400	0.920(23)
	0.0600	2.57(9)		0.0800	1.65(5)
	0.0850	2.99(3)		0.1024	2.06(2)
	0.1100	3.78(4)		0.1100	2.20(5)
	0.1403	4.20(3)		0.1400	2.75(4)
	0.1503	4.87(5)		0.1700	3.51(3)
	0.1700	5.82(10)		0.1900	3.81(2)
	0.1700	5.89(4)		0.2100	4.32(3)
	0.2000	6.55(6)		0.0289	1.48(2)
	0.2300	6.89(13)		0.0500	2.67(3)
Cr(I) 125.0	0.0201	1.60(1)	W(Br) 110.0	0.0672	3.39(3)
	0.0503	2.29(2)		0.1018	5.19(3)
	0.0903	3.08(4)		0.1150	6.39(5)
	0.1304	4.16(4)		0.1300	6.97(3)
	0.1614	4.92(4)		0.1800	9.00(14)
	0.2091	5.62(5)		0.2400	12.2(1)
				0.3000	15.5(2)
				0.0241	3.30(3)
				0.0625	8.28(4)
				0.0987	13.3(1)
Mo(Br) 55.0	0.00985	0.444(3)	W(I) 120.0	0.1300	17.2(1)
	0.0202	0.869(7)		0.1500	19.5(1)
	0.0303	0.974(13)		0.1700	22.6(2)
	0.0400	1.57(1)		0.1700	22.7(1)
	0.0800	2.73(2)		0.2000 ^a	24.4(1)
	0.1200	4.03(5)		0.2352 ^a	27.6(6)
	0.1600	5.33(6)		0.2400 ^a	27.4(2)
	0.2000 ^a	6.44(8)		0.2700 ^a	31.6(3)
	0.2400 ^a	7.41(6)		0.3000 ^a	36.2(3)
	0.2400 ^a	7.41(3)			
0.2800 ^a	9.15(10)				
W(Cl) 95.0	0.0314	1.49(2)		0.0200	0.688(18)
	0.0622	2.82(3)		0.0400	1.43(2)
	0.0816	3.39(2)		0.0600	2.00(3)
	0.1166	4.67(4)		0.0800	2.41(1)
	0.1388	6.15(7)		0.1003	3.43(3)
	0.1543	6.53(5)		0.1200	3.85(6)
				0.1300	4.25(3)
				0.1600 ^a	4.99(6)

^a Not employed in the determination of rate constants; see text.

the path involving rate-determining dissociation of CO more accessible; reactions of Mn(CO)₅X with X⁻ proceed under considerably milder conditions (ca. 25-40°) than do the corresponding reactions of X⁻ with M(CO)₆ [5].

For several systems (W-Br and W-I at 120.0° and Mo-Br), small but significant negative deviations from linearity of plots of k_{obs} vs. [Bu₄NX] were observed at high halide concentrations (Fig. 1). Such data, while listed in Table 1 (marked with an a), were not employed in the determination of the rate constants. No explanation for such behavior is evident, particularly in view of its appearance in some systems but not in others.

For reaction of tetrabutylammonium bromide with tungsten hexacarbonyl, the calculated entropy of activation (Table 2) is, within experimental error, zero,

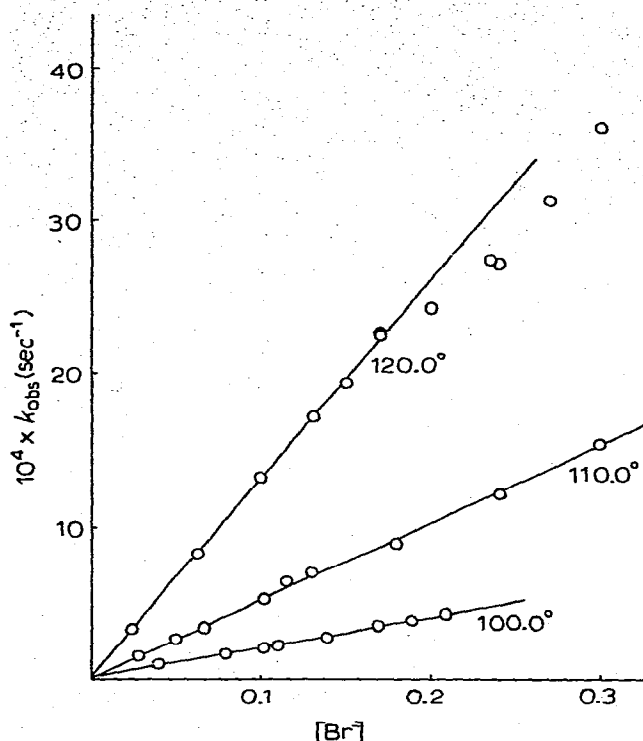


Fig. 1. Plots of k_{obs} vs. $[\text{Bu}_4\text{NBr}]$ for reaction of $\text{W}(\text{CO})_6$ with tetrabutylammonium bromide in chlorobenzene at three different temperatures.

not unreasonable in view of the relatively non-polar solvent employed. In such a solvent it is to be expected that the tetrabutylammonium halide will exist as a contact ion-pair; thus some separation of that ion-pair can occur synchronously with formation of the halide-substrate bond.

Information with regard to the site of halide attack at the substrate may be obtained through comparisons of rates (or activation parameters) for reactions via associative paths in which it is probable that nucleophilic attack occurs at a

TABLE 2

FIRST AND SECOND ORDER RATE CONSTANTS AND ACTIVATION PARAMETERS FOR REACTIONS OF METAL HEXACARBONYLS WITH TETRABUTYLAMMONIUM HALIDES

Metal	Halide	T (°C)	$10^4 \times k_1$ (sec^{-1})	$10^4 \times k_2$ ($\text{mol}^{-1} \cdot \text{sec}^{-1}$)
Cr	Br	120.0	0.60(22)	28.9(16)
Cr	I	125.0	1.19(13)	22.0(9)
Mo	Br	55.0	0.15(6)	32.4(7)
W	Cl	95.0	0.14(22)	41.4(20)
W ^a	Br ^a	100.0	0.05(6)	20.0(5)
		110.0	0.10(14)	51.0(9)
		120.0	0.09(20)	131.9(16)
W	I	120.0	0.07(11)	32.0(13)

^a $\Delta H_2^\ddagger = 26.5(4)$ kcal/mole; $\Delta S_2^\ddagger = -0.3(10)$ cal/deg-mole.

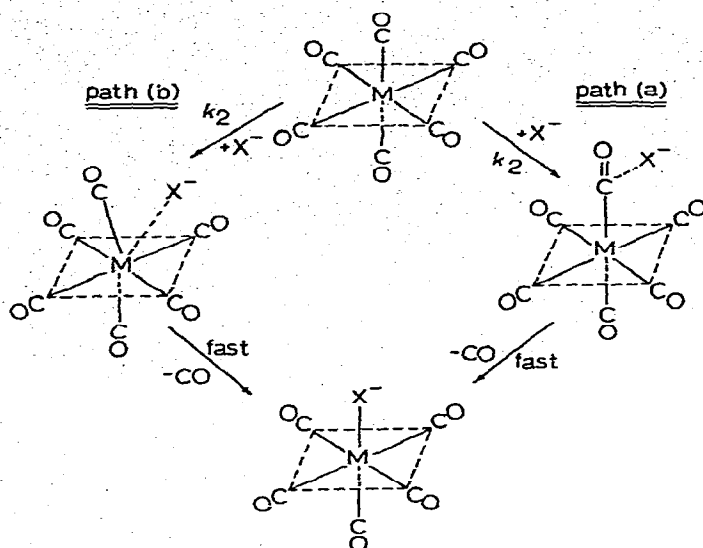


Fig. 2. Possible associative paths for reaction of metal hexacarbonyls with halides.

carbonyl carbon (path a, Fig. 2) or at the metal atom (path b, Fig. 2). Such systems include reactions of the hexacarbonyls with the azide ion to afford isocyanate products (path a) [8] and the corresponding reactions with Lewis bases, e.g., tributylphosphine, for which relative rates as a function of the identity of the metal atom suggest a different associative path, most probably involving attack at the metal atom [7]. Activation parameters for these reactions, together with the differences in the enthalpies of activation, are shown in Table 3. It is of interest to note that the relative enthalpies of activation for reactions of $\text{Cr}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$ via both paths are similar, but those for $\text{W}(\text{CO})_6$ differ appreciably. The differences can be rationalized on the basis of results of normal coordinate analyses for the hexacarbonyls based on use of a general quadratic force field [13]. The magnitude of the carbonyl and metal-carbon stretching force constants indicate stronger $\text{OC}-\text{W}$ σ -bonding than $\text{OC}-\text{Mo}$ or $\text{OC}-\text{Cr}$ σ -bonding. Thermochemical and electron impact data also support a greater $\text{W}-\text{C}$ bond strength [14]. Increased $\text{W}-\text{C}$ σ -bonding should effectively transfer charge from the carbonyl carbon to the metal, increasing the relative rate of nucleophilic attack at carbon, as observed.

TABLE 3

ENTHALPIES OF ACTIVATION (IN KCAL/MOLE) FOR REACTIONS OF METAL HEXACARBONYLS VIA TWO DIFFERENT ASSOCIATIVE PATHS

Substrate	Nucleophile		
	$\text{P}(\text{n}-\text{C}_4\text{H}_9)_3$ ^a	$[(\text{C}_2\text{H}_5)_4\text{N}]\text{N}_3$ ^b	Difference
$\text{Cr}(\text{CO})_6$	25.5(29)	18.2(6)	6.3(35)
$\text{Mo}(\text{CO})_6$	21.7(13)	15.3(8)	6.4(21)
$\text{W}(\text{CO})_6$	29.2(16)	12.8(10)	16.4(26)

^a Ref. 7. ^b Ref. 8.

Since steric factors are roughly equal in $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ (for which the metal atoms have roughly the same covalent radii) [15], the variations in rate for these substrates in their reactions with other nucleophiles provide evidence as to the site of attack by tetrabutylammonium halides. The observed relative rates ($\text{Mo} \gg \text{W}$) are similar to those observed for these metals in reactions with Lewis bases [7], but are substantially different from those observed where nucleophilic attack at a carbonyl carbon is the preferred reaction pathway ($\text{W} > \text{Mo}$) [8]. On this basis attack by the halides at the Mo or W atom is the favored mechanism. However, reactivity of $\text{Cr}(\text{CO})_6$ is substantially less than might be expected based on kinetic data for attack at the metal atom [7]. This is understandable in terms of the smaller covalent radius of Cr than of Mo or W, and the greater steric demands of the halide ions relative to phosphines. The diminution or lack of reactivity via an associative path for first row octahedral metal carbonyls relative to the analogous second or third row complexes has been noted [16], and has been attributed to such a steric influence. It is relevant to cite the non-polar covalent radius of P (1.06 Å) and the apparent ionic radii of Cl^- , Br^- and I^- (1.81, 1.95, and 2.16 Å, respectively) [17] in support of a decreased reactivity of the halides relative to phosphines with $\text{Cr}(\text{CO})_6$. A consideration of the relative molecular geometries of the phosphines and halides confirms the greater steric demands of the latter in their interactions at the chromium atom.

Should attack in $\text{Cr}(\text{CO})_6$ occur at the metal atom, a greater discrimination in rate between Br^- and I^- for $\text{Cr}(\text{CO})_6$ than for $\text{W}(\text{CO})_6$ is to be anticipated. However, the observation is (Table 2) that $\text{W}(\text{CO})_6$ rather than $\text{Cr}(\text{CO})_6$ is more sensitive to nucleophile size effects. Tentatively it may be suggested that in $\text{Cr}(\text{CO})_6$, steric effects preclude reaction via path b (Fig. 2) and that the halide-dependent rate observed for $\text{Cr}(\text{CO})_6$ may be attributable to path a (Fig. 2).

Should this indeed be the case, it is not unreasonable to expect facile formation of haloacyl intermediates from $[\text{Fe}(\text{CO})_5 \text{X}] \text{X}$ as proposed by Noack (eqn. 2) [9] in view of the expected smaller size of the unipositive Fe atom, which should inhibit attack at the metal; increased positive charge at a carbonyl carbon in the Fe substrate should facilitate halide attack at that site.

For a given metal atom, rates of reaction vary $\text{Cl}^- > \text{Br}^- > \text{I}^-$. While it has been observed that the relative nucleophilicities of the halides are strongly dependent on the nature of the solvent and that in less polar solvents (such as chlorobenzene) reactivities are more likely to parallel substrate-halide bond strengths [18], information with regard to those strengths is lacking. Hieber and Wollmann have studied the exchange of halides in $\text{Mn}(\text{CO})_5 \text{X}$ and *cis*- $\text{Fe}(\text{CO})_4 \text{X}_2$ complexes ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) with the corresponding radioactive halogens which proceed via a halogen-independent rate law [19], but the results reveal little about relative M-X bond strengths, particularly in view of the widely divergent (and, in some instances, highly negative) entropies of activation calculated from their data [20], and the lack of reactivity trends as a function of X from metal to metal. Thus, at the present time, detailed discussion of the observed trends would be premature, save to note that the observed order is consistent with the steric properties of the halides.

Acknowledgements

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