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Octahedral Metal Carbonyls. XXXVII.[a] The Kinetics and Mechanism of Reactions of Amines with the Group VI-B Metal Carbonyls

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Studies of the rates of reaction of the Group VI-B metal hexacarbonyls (M = Cr, Mo, W) with benzylamine, cyclohexylamine and aniline (amine) support a rate law, $-d[M(CO)_6]/dt = k_1[M(CO)_6] + k_2[M(CO)_6][amine]$. *The rate law is suggestive of two competing mechanisms, with the amine-independent path involving rate-determining dissociation of CO followed by amine uptake (D). The remarkable parallelism in rates for the competing processes for all three metals suggests the same factors to influence the rate of reaction by each path. Activation parameters for reaction of* $Mo(CO)_6$ *with benzylamine, and the relative insensitivity of the rate to the identity of a wide variety of incoming nucleophiles for the amine-dependent path support a mechanism* (I_d)*, in which M–CO bond breaking is very important. Comparisons of second-order rate constants for reactions of amines, and phosphines and phosphites indicate relatively little* π*-interaction in the transition state for substitution reactions of the latter.*

Introduction

The kinetics and mechanism of reactions of the Group VI-B metal carbonyls ($M(CO)_6$, M = Cr, Mo, W) with amines and with other nucleophiles have been investigated by Werner and Prinz [1]. The data supported a rate law,

$$-d[M(CO)_6]/dt = k_1[M(CO)_6] \tag{1}$$

consistent with a dissociative (D) [2] mechanism involving rate-determining fission of a M–C bond, followed by rapid attack by the ligand at the resulting five-coordinate intermediate:

$$M(CO)_6 \xrightarrow[-CO]{k_1} [M(CO)_5] \xrightarrow[+amine]{fast} M(CO)_5(amine) \tag{2}$$

The data of Werner and Prinz for primary amines (non-sterically-demanding) were, however, taken over a concentration range (10^{-4}–8×10^{-2} *M*) such that a ligand-dependent path might not be observed if not predominant.

Later, Angelici and Graham, in investigating the kinetics and mechanism of reactions of the hexacarbonyls with phosphines and phosphites (L) over a much wider range of concentrations observed the rate law [3],

$$-d[M(CO)_6]/dt = k_1[M(CO)_6] + k_2[M(CO)_6][L] \tag{3}$$

The second-order term in the rate law was attributed to nucleophilic attack by L at the substrate (either at the metal atom, or at a carbonyl carbon) followed by other steps:

$$M(CO)_6 \xrightarrow[+L]{k_2} [M(CO)_6(L)] \xrightarrow[fast]{-CO} M(CO)_5(L) + CO \tag{4}$$

Subsequent work has suggested attack at the metal atom to be more probable [4].

The question of the nature of the process responsible for the ligand-dependent path in reactions of octahedral metal carbonyls has prompted a further investigation of the kinetics and mechanism of their reactions with amines. Results of Covey and Brown for reactions of (amine)$Mo(CO)_5$ complexes with various nucleophiles have been interpreted as indicating that the "associative" path is best described as a "dissociative interchange" (I_d) process [2] in which there is relatively little bond-making in the transition state [5]. Such a process should afford a ligand-dependent term for a wide range of nucleophiles. Indeed, a recent study has revealed such a term for reaction of the hexacarbonyls with acetonitrile [6]; Lewis bases coordinating through nitrogen have been observed to be relatively poor nucleophiles in their reactions with metal carbonyls.

On the other hand, a traditional view of the associative process in reactions of metal carbonyls has held that significant stabilization of the transition

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[a] Part XXXVI: L. D. Schultz and G. R. Dobson, *J. Coord. Chem.*, *5*, 163 (1976). [b] Robert A. Welch Predoctoral Fellow, 1972–1976.

state through metal-to-ligand π-bonding takes place [7], and on this basis a ligand-dependent term in the rate law would not be anticipated for amines. For these reasons, and because it is desirable to have detailed rate data for reactions of the hexacarbonyls with nucleophiles exhibiting as wide a range of bonding properties as possible [8], rates of reaction of amines with these substrates have been studied over a broader concentration range.

Experimental

Materials

Reactions of the hexacarbonyls with amines in decalin were found to be extremely sensitive to traces of impurities, and thus, rigorous purification of reagents was carried out. The hexacarbonyls were obtained from Pressure Chemical Company ($Cr(CO)_6$ and $W(CO)_6$) and Climax Molybdenum ($Mo(CO)_6$) and were purified by sublimation under high vacuum (*ca.* 0.05 torr) at room temperature ($Cr(CO)_6$ and $Mo(CO)_6$) or 40 °C ($W(CO)_6$). They were then stored under nitrogen in foil-wrapped vials in a desiccator. They were occasionally placed under high vacuum briefly to insure dryness.

Cyclohexylamine was obtained from Matheson, Coleman and Bell, and benzylamine from the J.T. Baker Chemical Company. The ligands were purified through adapatation of methods employed in the rigorous purification of aniline [9–11].

Cyclohexylamine was refluxed overnight with 10 per cent acetone, diethyl ether was added, and the solution was acidified (concentrated HCl) until two phases were present. The cyclohexylamine was then repeatedly extracted with diethyl ether until the last ether extraction was colorless. The aqueous layer was then further acidified, and the precipitated $C_6H_{11}NH_3^+Cl^-$ was filtered, washed with ether, and was five times recrystallized from 95 per cent ethanol. The purified salt was then added to a saturated aqueous KOH solution and the liberated amine, which contained water, was distilled at atmospheric pressure (91 °C). The amine was separated, water again was added, and the distillation was repeated. The amine again was separated, and dried over anhydrous $CaCl_2$. It was then dried over sodium under nitrogen, and redistilled (six times, 133–4 °C) under an atmosphere of nitrogen which had been passed over anhydrous calcium chloride [12].

Benzylamine was purified in much the same manner; the distillations were carried out under reduced pressure (69 °C, 10 torr, dry nitrogen bleed). Potassium hydroxide, rather than calcium chloride, was employed as a drying agent.

Aniline was also purified through use of similar procedure, but it was not possible to obtain this ligand in sufficient purity to afford reproducible rate data (see below). Nonetheless, the attempts for reaction with $Mo(CO)_6$ did indicate the presence of a second-order reaction path with this ligand.

The ligands were kept under vacuum between and after distillations lest exposure to air result in the presence of hydrogen-bonded water and the formation of amine oxide.

Tri(isopropyl) phosphite (Aldrich) was purified as previously described [13].

Decalin (Pfaltz and Bauer, Inc.) was vacuum-distilled over sodium (68 °C, 12 torr) three times, and was stored under dry nitrogen.

Determination of Reaction Rates

Rates of reaction were determined employing a Perkin–Elmer Model 621 grating spectrophotometer under pseudo first-order reaction conditions (at least a twelve-fold excess of amine) through observation of the decrease in intensity of the T_{1u} carbonyl stretching mode of the substrate at the appropriate frequency (1985–1990 cm^{-1}) [14]. Hexacarbonyl concentrations employed were approximately 5×10^{-4} molar (0.5 mm pathlength). The amine was distilled twice immediately prior to each run and was then placed in a nitrogen filled glove bag for transfer to a 25 ml weighed volumetric flask. The flask was closed, removed from the glove bag, weighed, placed in a constant temperature bath at the reaction temperature, and brought to volume with solvent under a nitrogen purge. The substrate was placed in a separate volumetric flask (50 ml), and the flask was then flushed with nitrogen and sealed with a rubber septum. The equilibrated solvent–ligand solution was then injected into the reaction flask after removal of an equal volume of nitrogen from that flask, employing a large syringe. After re-equilibration for at least twenty minutes, sampling of the reaction solution was effected employing conventional techniques [15].

Several runs were carried out employing gas-tight syringes as reaction vessels to eliminate the gas phase above the reaction solution [3, 4], but these results indicated that possible sublimation of the hexacarbonyls and/or gas phase reactions were of negligible influence on the observed reaction rates.

The ligand and reaction products were found not to absorb significantly at the wavelengths monitored, so values of absorbance at t_∞ were not taken, since 0 to 100 per cent transmittance values were set on the spectrophotometer with solvent in each cell. Plots of ln(absorbance) *vs.* time, which afforded the pseudo first-order rate constants, k_{obsd}, were linear to at least four half-lives. Data were analyzed employing a least-squares computer program on an IBM 360 model 50 computer. Limits of error (uncertainty of last digit(s)) are one standard deviation.

TABLE I. Rates of Reaction of the Group VI-B Metal Hexacarbonyls (M = Cr, Mo, W) with Cyclohexylamine, Benzylamine, and Tri(isopropyl) Phosphite in Decalin.

Nucleophile, L	*M*	T, °C	[L], *M*	$10^4 k_{obsd}$, sec^{-1}
$C_6H_5CH_2NH_2$	Cr	130.00(5)	0.0141	1.22(2)
			0.0145	1.296(7)
			0.0170	1.24(1)
			0.0468	1.34(1)
			0.0503	1.24(3)
			0.0612	1.249(3)
			0.0784	1.24(2)
			0.1261	1.34(4)
			0.1264	1.33(1)
			0.1304	1.41(1)
			0.1341	1.41(2)
			0.1534	1.36(1)
			0.1628	1.43(1)
			0.1754	1.41(2)
			0.1973	1.37(1)
			0.2156	1.385(7)
			0.2468	1.385(8)
			0.2636	1.461(8)
$C_6H_{11}NH_2$	Mo	112.00(5)	0.0053	2.36(2)
			0.0332	2.542(8)
			0.0367	2.62(6)
			0.0524	2.657(6)
			0.0596	2.55(1)
			0.0786	2.78(1)
			0.0851	2.65(5)
			0.1119	2.78(2)
			0.1283	2.90(2)
			0.1313	3.00(3)
			0.1352	2.96(3)
			0.1464	3.05(3)
			0.1478	3.06(2)
			0.1479	3.00(1)
			0.1609	3.05(3)
			0.1837	3.16(3)
			0.2209	3.21(2)
			0.2332	3.27(2)
			0.2605	3.61(2)
			0.2655	3.48(2)
			0.2803	3.61(2)
$C_6H_5CH_2NH_2$	Mo	102.00(5)	0.0226	0.708(8)
			0.0512	0.763(4)
			0.0901	0.826(7)
			0.1065	0.867(7)
			0.1651	0.960(9)
			0.1888	0.992(4)
			0.2323	1.065(4)
			0.2536	1.094(5)
			0.2949	1.18(4)
$C_6H_5CH_2NH_2$	Mo	102.00(5)	0.2959	1.16(4)
			0.3184	1.21(10)
		107.00(5)	0.0370	1.28(3)
			0.0619	1.41(1)
			0.0626	1.36(2)
			0.0738	1.45(1)
			0.0774	1.44(2)
			0.0909	1.51(3)
			0.1297	1.62(1)
			0.1467	1.66(2)
			0.2110	1.854(7)
			0.2220	1.801(5)
			0.2222	1.851(7)
		112.00(5)	0.0118	2.61(12)
			0.0179	2.45(1)
			0.0183	2.49(2)
			0.0410	2.53(4)
			0.0548	2.85(2)
			0.0563	2.61(2)
			0.0696	2.73(1)
			0.0909	2.78(1)
			0.1044	2.948(5)
			0.1165	3.01(5)
			0.1289	3.00(2)
			0.1795	3.21(3)
			0.1901	3.40(5)
			0.2139	3.28(3)
			0.2169	3.34(4)
			0.2299	3.40(5)
			0.2717	3.74(6)
$((CH_3)_2CHO)_3P$	Mo	112.00(5)	0.00658	2.52(3)
			0.04171	2.58(4)
			0.05878	2.67(4)
			0.08860	2.60(3)
			0.11657	2.88(3)
			0.14145	2.81(3)
$C_6H_5CH_2NH_2$	W	150.00(5)	0.0173	0.247(3)
			0.0213	0.262(2)
			0.0484	0.263(6)
			0.0800	0.277(5)
			0.1282	0.290(2)
			0.1514	0.301(2)
			0.1729	0.299(3)
			0.1844	0.306(4)
			0.2182	0.314(5)
			0.2257	0.324(1)
			0.2371	0.330(4)
			0.2841	0.341(4)

Identification of Reaction Products

Scans of the infrared spectra of reaction solutions as a function of time reveal the initial formation of the (amine)M$(CO)_5$ products, followed by further substitution.

Most of the (amine)M$(CO)_5$ complexes are known [16–19], and they exhibit well-documented [19, 20] and characteristic carbonyl stretching spectra in hydrocarbon solvent. The initial reaction product of tri(isopropyl)phosphite and Mo$(CO)_6$ was identified

TABLE II. First and Second Order Rate Constants, and Activation Parameters for Reactions of the Group VI-B Metal Hexacarbonyls with Amines and Tri(isopropyl) Phosphite in Decalin.

Substrate	Nucleophile (L)	T, °C	10^4k_1 (sec^{-1})	10^4k_2 ($M^{-1}sec^{-1}$)
$Cr(CO)_6$	$C_6H_5CH_2NH_2$	130.00(5)	1.24(2)	0.79(13)
$Mo(CO)_6$	$C_6H_{11}NH_2$	112.00(5)	2.38(3)	4.2(2)
	$C_6H_5CH_2NH_2$[a]	102.00(5)	0.677(5)	1.67(2)
		107.00(5)	1.22(2)	2.88(15)
		112.00(5)	2.44(4)	4.4(3)
	$((CH_3)_2CHO)_3P$	112.00(5)	2.49(6)	2.4(7)
$W(CO)_6$	$C_6H_5CH_2NH_2$	150.00(5)	0.248(3)	0.33(2)

[a] Activation parameters: $\Delta H_1^{\ddagger}$ = 36.0(29) kcal/mol; $\Delta S_1^{\ddagger}$ = 19.1(92) cal/deg mol. $\Delta H_2^{\ddagger}$ = 27.2(24) kcal/mol; $\Delta S_2^{\ddagger}$ = −3.7(62) cal/deg mol.

through comparison of its carbonyl stretching spectrum to those of closely-related $P(OR)_3Mo(CO)_5$ complexes [21].

Results and Discussion

Values for the pseudo first-order rate constants (k_{obsd}) are presented in Table I. In Table II are exhibited the rate constants, k_1 and k_2, obtained from plots of k_{obsd} *vs.* [amine], which obeyed the relationship,

$$k_{obsd} = k_1 + k_2[\text{amine}] \qquad (5)$$

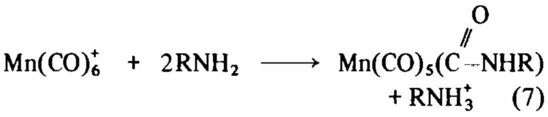
Activation parameters for reaction of $Mo(CO)_6$ with benzylamine in decalin at 102–112 °C are also given in Table II.

The plots of k_{obsd} *vs.* [amine] are consistent with rate law (3), which involves two competing reaction paths each leading, initially, to the simple substitution products,

$$M(CO)_6 + \text{amine} \longrightarrow M(CO)_5(\text{amine}) + CO \qquad (6)$$

The ligand-independent path governed by k_1 is best ascribed to rate-determining fission of a metal–carbon bond to afford a five-coordinate intermediate, followed by rapid uptake of amine (D mechanism [2], Eq. 2). This is a mechanism proposed for many related reactions [5, 7, 8]. Rates and activation parameters observed for the path governed by k_1 are in reasonable agreement with those observed previously for reactions of $M(CO)_6$ (M = Cr, Mo, W) with Lewis bases under similar reaction conditions [1, 3] (see Table III). It is probable that the intermediate resulting from metal–carbonyl bond fission exhibits square-pyramidal geometry [22].

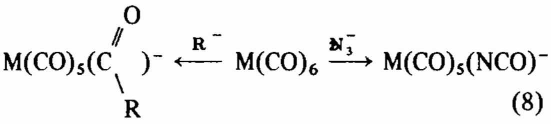
The term governed by k_2 in the observed rate law suggests participation by the amine in the rate-determining step. For reactions of Group VII-B metal octahedral cations and derivatives, reactions with primary amines afford carbamoyl derivatives [23], *e.g.*,



$$Mn(CO)_6^+ + 2RNH_2 \longrightarrow Mn(CO)_5(C(=O)NHR) + RNH_3^+ \qquad (7)$$

and it is almost certain that this process involves an initial interaction at carbon.

And while Group VI-B metal carbonyls react with strong nucleophiles such as carbanions derived from organolithiums and Grignard reagents, and azides to afford products which suggest interaction at carbon [24–26],



$$M(CO)_5(C(=O)R)^- \xleftarrow{R^-} M(CO)_6 \xrightarrow{N_3^-} M(CO)_5(NCO)^- \qquad (8)$$

their reactions with amines afford simple ligand-exchange products (Eq. 6), rather than carbamoyl derivatives (Eq. 7). Further, rates of reaction of Lewis bases and of amines *via* a ligand-dependent path vary Mo > Cr > W, not the order observed for systems in which attack at carbon is probable. Rates of reaction as a function of the identity of the metal atom should parallel one another if the same mechanism is applicable, and thus it is probable that in the present case attack does not occur at carbon [4].

It is observed in the present reactions and in other ligand-exchange processes involving Lewis bases [3, 6], that the magnitude of the second-order term in rate law (3) closely parallels that of the first-order term, and that the values of k_2 vary rather little among nucleophiles. Some of the relevant data are summarized in Table III. They indicate that the same factors which influence reactivity for the dissociative path also appear to be important for the ligand-dependent path. Thus it may be presumed that there

TABLE III. Rate Constants for Reactions of the Group IV-B Metal Hexacarbonyls with Various Lewis Bases (L), Decalin Solvent.

Substrate	T, °C	L	$10^4 k_1$ (sec^{-1})	$10^4 k_2$ ($M^{-1} sec^{-1}$)
$Cr(CO)_6$	130.7° [a]	$P(C_6H_5)_3$	1.38	0.431
	130.7° [a]	$P(OC_2H_5)_3$	1.38	0.450
	130.0° [b]	$C_6H_5CH_2NH_2$	1.24(2)	0.79(13)
	130.7° [a]	$P(n\text{-}C_4H_9)_3$	1.38	0.854
$Mo(CO)_6$	112.0° [a]	$As(C_6H_5)_3$	2.13	1.03
	112.0° [a]	$P(OC_6H_5)_3$	2.13	1.48
	112.0° [a]	$P(C_6H_5)_3$	2.13	1.77
	112.0° [b]	$P(OCH(CH_3)_2)_3$	2.49(6)	2.4(7)
	112.0° [a]	$P(OCH_2)_3CCH_3$	2.13	3.56
	112.0° [b]	$C_6H_{11}NH_2$	2.38(3)	4.2(2)
	112.0° [b]	$C_6H_5CH_2NH_2$	2.44(4)	4.4(3)
	112.0° [a]	$P(OC_2H_5)_3$	2.13	6.69
	112.0° [a]	$P(n\text{-}C_4H_9)_3$	2.13	20.5
	64.5° [c]	CH_3CN	0.0056	0.0229
	64.5° [c]	C_6H_5CN	0.0053	0.0287
$W(CO)_6$	165.7° [a]	$P(C_6H_5)_3$	1.15	0.888
	165.7° [a]	$P(OCH_2)_3CCH_3$	1.15	1.48
	165.7° [a]	$P(OC_2H_5)_3$	1.15	1.70
	165.7° [a]	$P(n\text{-}C_4H_9)_3$	1.15	7.10
	150.0° [b]	$C_6H_5CH_2NH_2$	0.33(2)	0.248(3)

[a] Reference 3; average values of k_1 are given. [b] This work. [c] Reference 6; $C_2H_2Cl_2$ solvent.

is appreciable bond-breaking in the transition state for this path, as was proposed by Covey and Brown [5] for ligand-exchange reactions of (amine)$Mo(CO)_5$ complexes. The path governed by k_2 may thus be considered to be a "dissociative interchange" (I_d) [2] process in which a properly-positioned L fills a coordination site vacated by a dissociating carbonyl. The applicability of the I_d mechanism in these systems is further supported by the rather small differences in the enthalpies of activation for the processes governed by k_1 and k_2. Based upon Hammond's postulate [27], these observations suggest little bond-making, whether by σ- or π-interaction, in the transition state leading to products.

By way of contrast, rate data for reaction of the hexacarbonyls with halides show a dramatic difference in rate *via* an "associative" path compared to the analogous reactions of phosphines, amines and other Lewis bases. Reaction of $W(CO)_6$ with tetra(n-butyl)ammonium bromide (chlorobenzene solvent) is some three orders of magnitude faster than with tri(n-butyl)phosphine [4]. This observation would seemingly indicate a significant difference in mechanism between these nucleophiles, although it has been proposed that in both cases the metal atom is the site of bimolecular interaction.

Acknowledgments

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