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Kinetics Studies of Carbon Monoxide Insertion Reactions. The Reactions of Cyclopentadienyl(methyl)iron Dicarbonyl and Cyclopentadienyl(methyl)molybdenum Tricarbonyl with Phosphines and Phosphites

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Received June 7, 1967

The rates of reaction of $C_5H_5Fe(CO)_2CH_3$ in tetrahydrofuran solution with various ligands to give $C_5H_5FeCO(COCH_3)L$ are reported where L = $P(C_6H_5)_3$, $P(n\text{-}C_4H_9)_3$, and $P(n\text{-}OC_4H_9)_3$. At low concentration the rates of reaction depend on ligand concentration but a limiting rate is reached at higher ligand concentrations. Kinetic data were also obtained for the corresponding reactions of $C_5H_5Mo(CO)_3CH_3$ in tetrahydrofuran and toluene solutions to yield $C_5H_5Mo(CO)_2(COCH_3)L$. The results can be explained on the basis of the solvent- and/or nucleophile-assisted mechanism described previously for the reaction of $CH_3Mn(CO)_5$.

Introduction

The results of kinetic studies of the so-called "carbon monoxide insertion reactions" of methylmanganese pentacarbonyl with amines and phosphines (eq 1) were

$$CH_3Mn(CO)_5 + L \longrightarrow CH_3COMn(CO)_4L \qquad (1)$$

successfully explained by a unified mechanism involving a solvent-assisted "methyl migration."[1,2] Although the evidence cited in support of methyl migration[3] is ambiguous,[4] the migration still appears to be a more plausible mechanism than does carbon monoxide insertion.[5]

Bibler and Wojcicki[6] found that cyclopentadienyl(methyl)iron dicarbonyl reacts with triphenylphosphine, triphenyl phosphite, tri-*n*-butylphosphine, and tri-*n*-butyl phosphite in refluxing tetrahydrofuran to give almost quantitative yields of the complexes $C_5H_5Fe(CO)(COCH_3)L$ (L = phosphine or phosphite). Prior to this the only ligand known to react with $C_5H_5Fe(CO)_2CH_3$ to give an acetyl derivative was carbon monoxide.[7] One of the most interesting observations made in the phosphine study was the considerable effect that the nature of the solvent had upon the reaction between $C_5H_5Fe(CO)_2CH_3$ and triphenylphosphine. In refluxing tetrahydrofuran (65°) the formation of the product was virtually complete in 48 hr; however, in refluxing hexane (68°) no reaction progress was detected over the same period of time. In boiling ether (34°) the reaction was about 50% complete in 48 hr.

The reaction of $C_5H_5Mo(CO)_3C_2H_5$ with carbon monoxide at 100 atm and 100° gives two products.[8] One is the expected propionyl compound $C_5H_5Mo(CO)_3(COC_2H_5)$ whereas the other is a dimeric species, $[(C_2H_5\cdot C_5H_4)Mo(CO)_3]_2$, formed by the migration of the ethyl group at temperatures above the melting point of the ethyl compound onto the cyclopentadienyl ring. Probably at lower temperatures only the propionyl product would be formed.

Recently, Barnett and Treichel[9] have reported that $C_5H_5Mo(CO)_3CH_3$ reacts with triphenylphosphine in donor and hydrocarbon solvents to yield mixtures of $C_5H_5Mo(CO)_2(COCH_3)P(C_6H_5)_3$ and $C_5H_5Mo(CO)_2(CH_3)P(C_6H_5)_3$. In tetrahydrofuran the initial compound formed is the acetyl derivative which then decarbonylates to give the methyl compound. The acetyl derivative has also been prepared independently in the present investigation.

This paper reports the results of a kinetic study of the reactions of $C_5H_5Fe(CO)_2CH_3$ and of $C_5H_5Mo(CO)_3CH_3$ with phosphines and phosphites in a variety of different solvents.

Experimental Section

Preparation and Purification of Materials.—The substrates $C_5H_5Fe(CO)_2CH_3$[10] and $C_5H_5Mo(CO)_3CH_3$[11] were prepared from the dimeric carbonyls $[C_5H_5Fe(CO)_2]_2$ and $[C_5H_5Mo(CO)_3]_2$ (obtained from Alfa Inorganics Inc.) by the methods described in the literature.

Tri-*n*-butylphosphine, tri-*n*-butyl phosphite, and triphenyl phosphite were fractionally distilled under nitrogen before use Triphenylphosphine (obtained from Eastman Kodak Co.) was used without further purification.

Tetrahydrofuran,[12] dimethylformamide,[13] and nitromethane[14] were purified as described in the literature and stored under nitrogen. Toluene was distilled from sodium under nitrogen.

Kinetic Studies.—The rates of the reactions for both compounds were followed by observing changes in the infrared spectra in the CO stretching region of the reaction mixtures. The reactions were generally followed by observing the rate of disappearance of the high-frequency bands at 2005 and 2020 cm^{-1} for $C_5H_5Fe(CO)_2CH_3$ and $C_5H_5Mo(CO)_3CH_3$, respectively. On a few occasions the rate of formation of product was followed by observing the rate of appearance of the product bands in both the metal- and the acetyl-carbonyl stretching regions of the

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[1] R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 3994 (1964).

[2] F. Calderazzo and F. A. Cotton, *Chim. Ind.* (Milan), **46**, 1165 (1964).

[3] R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 5043 (1964).

[4] (a) F. Calderazzo and K. Noack, *J. Organometal. Chem.* (Amsterdam), **4**, 250 (1965); (b) C. S. Kraihanzel and P. K. Maples, *J. Am. Chem. Soc.*, **87**, 5267 (1965).

[5] F. Calderazzo and F. A. Cotton, "Proceedings of the 7th International Conference on Coordination Chemistry," Stockholm, 1962, p 296.

[6] J. P. Bibler and A. Wojcicki, *Inorg. Chem.*, **5**, 889 (1966).

[7] T. H. Coffield, J. Kozikowski, and R. D. Closson, Special Publication No. 13, The Chemical Society, London, 1959, p 126.

[8] J. A. McCleverty and G. Wilkinson, *J. Chem. Soc.*, 4096 (1963).

[9] K. W. Barnett and P. M. Treichel, *Inorg. Chem.*, **6**, 294 (1967).

[10] T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

[11] J. J. Eisch and R. B. King, "Organometallic Syntheses," Academic Press Inc., New York, N. Y., 1965, p 145.

[12] K. A. Keblys and A. H. Filbey, *J. Am. Chem. Soc.*, **82**, 4204 (1960).

[13] G. R. Leader and J. F. Gormley, *ibid.*, **73**, 5731 (1951).

[14] R. J. Angelici and F. Basolo, *ibid.*, **84**, 2495 (1962).

spectrum. It was found for both compounds that the product formation took place at the same rate, within experimental error, as the rate of disappearance of the starting material.

All of the kinetic studies were carried out under pseudo-first-order conditions, using at least a tenfold excess of reagent. Light and air were excluded at all times.

The infrared data were obtained with a Perkin-Elmer 337 spectrophotometer equipped with a Servo/Riter expanded-scale recorder. Sodium chloride (1.0-mm) or potassium bromide (0.2-mm) cells were used for all solvents except dimethylformamide, in which case 0.2-mm barium fluoride cells were used. The kinetic measurements were carried out as discussed previously.[15] The rates are considered to be accurate to ±10% or better.

The infrared spectra in the CO stretching region of the products $C_5H_5Fe(CO)(COCH_3)L$ and $C_5H_5Mo(CO)_2(COCH_3)L$ are given in Table I. The spectra were calibrated with polystyrene film and are considered to be accurate to ±2.0 cm^{-1}.

TABLE I

CO STRETCHING FREQUENCIES (CM^{-1}) IN THE COMPOUNDS $C_5H_5Fe(CO)(COCH_3)L$ AND $C_5H_5Mo(CO)_2(COCH_3)L$ IN TETRAHYDROFURAN

	Ligand L	ν_{CO}	ν_{CO}(acetyl)
$C_5H_5Fe(CO)(COCH_3)L$	$P(n\text{-}C_4H_9)_3$	1911 vs, br	1601 s
	$P(n\text{-}OC_4H_9)_3$	1937 vs, br	1609 s
	$P(C_6H_5)_3$	1917 vs, br	1598 s
$C_5H_5Mo(CO)_2(COCH_3)L$	$P(n\text{-}C_4H_9)_3$	1940 s, 1860 vs	1600 m
	$P(n\text{-}OC_4H_9)_3$	1943 s, 1864 vs	1632 m
	$P(C_6H_5)_3$[a]	1941 s, 1860 vs	1629 m
	$P(OC_6H_5)_3$	1950 s, 1876 vs	1650 m

[a] In chloroform solution, the values are 1941 s, 1857 vs, and 1608 m cm^{-1}.

Product Identification.—The complex $C_5H_5Fe(CO)(COCH_3)P(C_6H_5)_3$ was prepared by the method of Bibler and Wojcicki[6] and was found to melt at 143° (lit. mp 145°). The infrared spectrum was in agreement with the published spectrum. The other iron acetyl derivatives were identified solely by their infrared spectra.

No reaction was observed between $C_5H_5Fe(CO)_2CH_3$ and cyclohexylamine in tetrahydrofuran at 50.7° for a period of 3 weeks.

The compound $C_5H_5Mo(CO)_2(COCH_3)P(C_6H_5)_3$ was isolated from a reaction mixture of $C_5H_5Mo(CO)_3CH_3$ (0.20 g) and triphenylphosphine (0.25 g) in tetrahydrofuran (10 ml). The reaction was carried out under nitrogen at 60° for 3 hr. Solvent was then removed under vacuum (~20 mm) to leave a yellow residue. This was then washed repeatedly with diethyl ether to remove excess triphenylphosphine and then recrystallized from chloroform–petroleum ether (bp 40–60°) mixtures; yield 70%, mp 153–154° (uncorrected). This is to be compared with a decomposition temperature of 147° reported previously.[9]

Anal. Calcd for $C_{27}H_{23}MoO_3P$: C, 62.07; H, 4.44. Found: C, 62.05; H, 4.66.

Yellow oils, which failed to crystallize, were isolated from the reactions of $C_5H_5Mo(CO)_3CH_3$ with tri-*n*-butylphosphine, tri-*n*-butyl phosphite, and triphenyl phosphite. However, the fact that the changes in the infrared spectra during the reactions were similar to those for the reaction with triphenylphosphine is strong evidence for the formation of similar acetyl complexes. No reaction was observed between $C_5H_5Mo(CO)_3CH_3$ and tetra-*n*-butylammonium iodide in tetrahydrofuran at 50.7° over a period of 1 week.

TABLE II

THE REACTIONS OF $C_5H_5Fe(CO)_2CH_3$ WITH TRI-*n*-BUTYLPHOSPHINE, TRI-*n*-BUTYL PHOSPHITE, AND TRIPHENYLPHOSPHINE IN TETRAHYDROFURAN AT 50.7°

Nucleophile L	Nucleophile concn, [L], *M*	10^6k_{obsd}, sec^{-1}	Nucleophile L	Nucleophile concn, [L], *M*	10^6k_{obsd}, sec^{-1}
$P(n\text{-}C_5H_9)_3$	0.971	2.74	$P(n\text{-}OC_4H_9)_3$	0.907	2.08
	0.657	2.54		0.726	2.09
	0.526	2.43		0.478	1.90
	0.361	1.91		0.301	1.41
	0.289	1.69		0.126	0.85
	0.246	1.56	$P(C_6H_5)_3$	0.856	2.73
	0.085	0.74		0.669	2.60
	0.101[a]	*b*		0.483	2.40
	0.910[c]	0.70		0.360	2.02
				0.222	1.52
				0.157	1.23
				0.095	0.80
				0.676[d]	2.78

[a] Reaction at 25°. [b] Negligible reaction after 1 week. [c] Reaction at 40.4°. [d] Rates of appearance of product by following the bands at 1917 and 1598 cm^{-1} are 2.58 and 2.50 × 10^{-6} sec^{-1}, respectively.

TABLE III

THE REACTIONS OF $C_5H_5Mo(CO)_3CH_3$ WITH VARIOUS NUCLEOPHILES IN TETRAHYDROFURAN

Nucleophile L	Nucleophile concn, [L], *M*	Temp, °C	10^4k_{obsd}, sec^{-1}	10^4k_{obsd},[a] sec^{-1}	
$P(n\text{-}C_4H_9)_3$	0.693	50.7	6.08		
	0.251		4.41		
	0.163		4.25		
$P(C_6H_5)_3$	0.806		4.02	4.26	(3.84)[b]
	0.487		3.71	*c*	
	0.312		3.36	*c*	
	0.225		3.83	4.32	(4.24)
	0.137[d]		3.33	4.46	(4.56)
	0.0912		3.78	4.89	(4.95)
	0.090		3.85	5.02	(4.96)
	0.0534		3.44	6.70	(5.66)
	0.0199		*e*	7.38	(7.29)
$P(n\text{-}OC_4H_9)_3$	0.235		4.17		
	0.796		3.17		
	0.245	35.15	1.09		
	0.151		1.09		
	0.439	25.0	0.419		
	0.180		0.419		
$P(OC_6H_5)_3$	0.351	50.7	3.17		
	0.764		2.98		

[a] Rate of approach to equilibrium. [b] Calculated values for the rate of approach to equilibrium. The mean values of k_1 and k_4 used to calculate the ratios k_2/k_3 necessary to recalculate the values of k_{obsd} were 3.67 × 10^{-4} and 1.18 × 10^{-3} sec^{-1}, respectively. The mean value of k_2/k_3 used was 0.0162. [c] Not determined. [d] Rate of formation of product determined by following rate of appearance of the band at 1629 cm^{-1} is 3.90 × 10^{-4} sec^{-1}. [e] Too rapid to be measured by this method.

Results

The reactions of both $C_5H_5Fe(CO)_2CH_3$ and $C_5H_5Mo(CO)_3CH_3$ with phosphines and phosphites were all first order in substrate regardless of solvent used. The observed first-order rate constants for these reactions are listed in Tables II–IV. The reaction of triphenylphosphine with $C_5H_5Mo(CO)_3CH_3$ in tetrahydrofuran and toluene did not go to completion, and in some of the tables both the initial rate assuming complete reaction and the rate of approach to the equilibrium position are given.

Data on the activation parameters for various reactions are given in Table V.

Reactions of Cyclopentadienyl(methyl)iron Dicarbonyl.—The results listed in Table II show that the

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(15) H. G. Schuster-Woldan and F. Basolo, *J. Am. Chem. Soc.*, **88**, 1657 (1966).

Table IV

The Reactions of $C_5H_5Mo(CO)_3CH_3$ with Various Nucleophiles in Toluene at 50.7°

Nucleophile L	Nucleophile concn, [L], *M*	10^5k_{obsd}, sec^{-1}	Nucleophile L	Nucleophile concn, [L], *M*	10^5k_{obsd}, sec^{-1}
$P(n\text{-}C_4H_9)_3$	0.798	5.67	$P(n\text{-}OC_4H_9)_3$	1.03	5.48
	0.372	3.13		0.575	3.44
	0.186	1.82		0.406	2.58
$P(C_6H_5)_3$	0.690	2.18		0.183	1.50
	0.342	1.10		0.123	1.19
	0.137	0.470		0.793	68[a]
	0.0685	0.275		0.400	72[a]
				0.790	~8000[b]
			$P(OC_6H_5)_3$	1.14	0.951
				0.655	0.564
				0.202	0.200

[a] Nitromethane solvent. [b] Dimethylformamide solvent.

Table V

Comparison of Activation Parameters for Some Solvent-Assisted Methyl Migration Reactions (k_1 Path) in Tetrahydrofuran

Compound	Reagent	ΔH^*, kcal/mole	ΔS^*, eu
$CH_3Mn(CO)_5$[a]	Cyclohexylamine	16.6 ± 0.6	−17 ± 2
$C_5H_5Fe(CO)_2CH_3$	$P(n\text{-}C_4H_9)_3$	26.1 ± 0.6	−4 ± 2
$C_5H_5Mo(CO)_3CH_3$	$P(n\text{-}OC_4H_9)_3$	16.1 ± 0.6	−25 ± 2

[a] Data taken from ref 1.

rates of reaction of $C_5H_5Fe(CO)_2CH_3$ with triphenylphosphine, tri-*n*-butylphosphine, and tri-*n*-butyl phosphite in tetrahydrofuran depend on the concentration of the nucleophile. The observed rate constants, when plotted against nucleophile concentration, rise toward limiting values. A similar behavior was noted for the reactions of $CH_3Mn(CO)_5$ with triphenylphosphine and triphenyl phosphite in tetrahydrofuran and cyclohexylamine in methanol.[1] The mechanism proposed in this case involved a short-lived intermediate which is perhaps solvated. A similar mechanism for the iron compound could be written as

$$C_5H_5Fe(CO)_2CH_3 \xrightarrow[\text{slow}]{\text{solvent}} C_5H_5Fe(CO)(COCH_3)(\text{solvent}) \xrightarrow[L]{\text{fast}} C_5H_5Fe(CO)(COCH_3)L \quad (A)$$

Recently, Treichel, *et al.*,[16] have isolated a stable substitution product $C_5H_5Fe(CO)(CH_3)P(C_6H_5)_3$ from the reaction under ultraviolet light of $C_5H_5Fe(CO)_2CH_3$ with triphenylphosphine in refluxing petroleum ether (bp 90–100°). This substitution product is readily carbonylated to give the acetyl derivative $C_5H_5Fe(CO)(COCH_3)P(C_6H_5)_3$. In view of this they suggest that the formation of the acetyl derivative comes about by the carbonylation of this substitution product by carbon monoxide from both the substitution process and decomposition. For such a sequence of reactions, the rate of disappearance of starting material should take place at a rate different from that for the formation of acetyl product. Reference to Table II shows that, for this reaction in tetrahydrofuran, the two rates are the same within experimental error. In view of this and the fact that no reaction was detected in refluxing hexane over a period of 2 days,[6] we feel that the formation of the substitution product is a consequence of the reaction being carried out at an elevated temperature and under ultraviolet light. This means that our kinetic data are best explained by mechanism A.

Mechanism A can be rewritten as

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \underset{k_4}{\overset{k_3}{\rightleftharpoons}} C$$

A is the starting material, B the intermediate, and C the final product. Using the steady-state approximation for the concentration of the intermediate, the following expression is obtained for the rate of disappearance of starting material

$$-\frac{d[A]}{dt} = k_1[A] - k_2\left(\frac{k_1[A] + k_4[C]}{k_2 + k_3(L)}\right) \qquad (2)$$

If the rate constant for the reversion to starting material, k_2, becomes comparable in size to the rate constant for the reaction with phosphine or phosphite, k_3, there will be a competition for the intermediate, which will result in a dependence of the observed rate on phosphine or phosphite concentration. If eq 2 is simplified by ignoring k_4 (a reasonable assumption since the reactions appear to go to completion over the range of investigation), the following is obtained

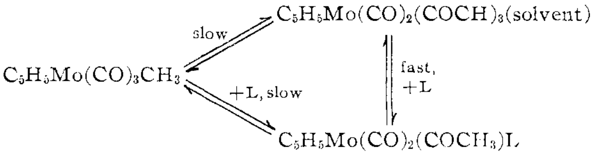
$$-\frac{d[A]}{dt} = \frac{k_1k_3[A][L]}{k_2 + k_3[L]} \qquad (3)$$

or

$$\frac{1}{k_{obsd}} = \frac{k_2}{k_1k_3}\left(\frac{1}{[L]}\right) + \frac{1}{k_1} \qquad (4)$$

In agreement with eq 4 straight lines were obtained on plotting $1/k_{obsd}$ against $1/[L]$ for all three nucleophiles (Figure 1). The values obtained for k_1 and the ratio k_2/k_3 are given in Table VI.

Reactions of Cyclopentadienyl(methyl)molybdenum Tricarbonyl in Different Solvents.—The results listed in Table III show that the rates of reaction of $C_5H_5Mo(CO)_3CH_3$ with triphenylphosphine, triphenyl phosphite, and tri-*n*-butyl phosphite in tetrahydrofuran are virtually independent of nucleophile concentration. However, with tri-*n*-butylphosphine there is a linear dependence on phosphine concentration, with a nonzero intercept corresponding to the reagent-independent rate. In the case of triphenylphosphine the reactions do not get to completion. Thus, the nature of the entering nucleophile is important in these reactions. One possible reaction scheme to explain this behavior involves a similar intermediate path to that discussed for the iron compound and a direct second-order path from starting material to product.



(B)

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(16) P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, **5**, 1177 (1966).

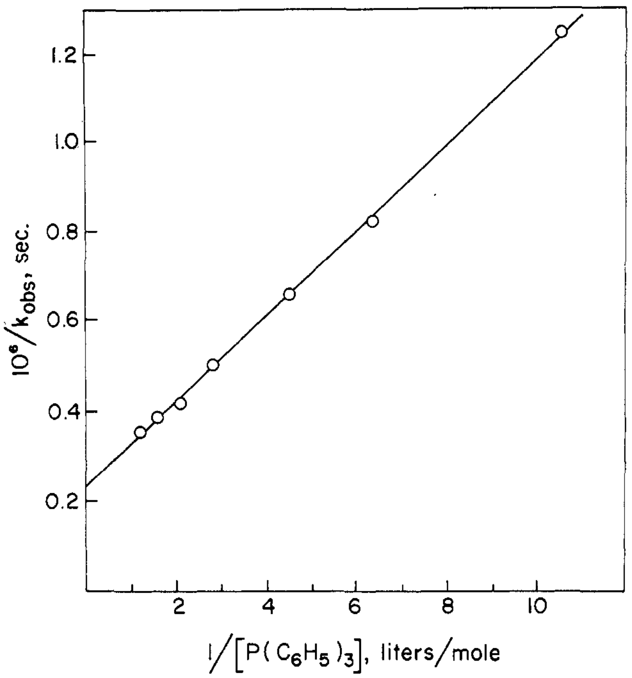


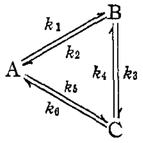
Figure 1.—Plot of the reciprocal of the observed rate constant *vs.* the reciprocal of the phosphine concentration for the reaction of $C_5H_5Fe(CO)_2CH_3$ with $P(C_6H_5)_3$ in tetrahydrofuran at 50.7°.

Table VI

Values of k_1 and k_2/k_3 Calculated from the Intercepts and Slopes, Respectively, of the Lines in Figure 2

Nucleophile L	10^6k_1, sec^{-1}	k_2/k_3, *M*
$P(n\text{-}C_4H_9)_3$	3.86	0.324
$P(n\text{-}OC_4H_9)_3$	3.35	0.382
$P(C_6H_5)_3$	4.18	0.396

Denoting the starting material, the intermediate, and the product by A, B, and C, respectively, the following is obtained



Applying the steady-state approximation for the concentration of the intermediate B, the following expression for the rate of disappearance of A is obtained

$$-\frac{d[A]}{dt} = k_1[A] - k_2\frac{k_1[A] + k_4[C]}{k_2 + k_3[L]} + k_5[A][L] - k_6[C] \qquad (5)$$

Let us first assume that the reactions go to completion. It is then justifiable to ignore k_4 and k_6 and to assume that $k_3[L]$ is much larger than k_2. Under these conditions eq 5 reduces to

$$-\frac{d[A]}{dt} = (k_1 + k_5[L])[A] \qquad (6)$$

This predicts a reaction that is first order in A and has an observed rate constant given by

$$k_{obsd} = k_1 + k_5[L] \qquad (7)$$

This equation is in agreement with the observed data for the reaction of tri-*n*-butylphosphine in tetrahydrofuran. The values obtained for k_1 and k_5 are shown in Table VII.

Table VII

Values of k_1 and k_5 for the Reactions of $C_5H_5Mo(CO)_3CH_3$ with Various Nucleophiles in Different Solvents at 50.7°

Solvent	Nucleophile L	k_1, sec^{-1}	k_5, M^{-1} sec^{-1}
Tetrahydrofuran	$P(n\text{-}C_4H_9)_3$	3.65×10^{-4}	3.49×10^{-3}
	$P(n\text{-}OC_4H_9)_3$	3.94×10^{-4}	
	$P(C_6H_5)_3$	3.67×10^{-4}	
	$P(OC_6H_5)_3$	3.10×10^{-4}	
Toluene	$P(n\text{-}C_4H_9)_3$	5.80×10^{-6}	6.44×10^{-5}
	$P(n\text{-}OC_4H_9)_3$	5.80×10^{-6}	5.00×10^{-5}
	$P(C_6H_5)_3$	...	3.22×10^{-5}
	$P(OC_6H_5)_3$	...	8.33×10^{-6}
Nitromethane	$P(n\text{-}OC_4H_9)_3$	6.99×10^{-4}	
Dimethylformamide	$P(n\text{-}OC_4H_9)_3$	$\sim 8.0 \times 10^{-2}$	

The reactions with the other nucleophiles used are independent of nucleophile concentration. Assuming mechanism B is correct, this means that these reactions proceed only by way of the solvent path. Consequently, we may ignore k_5 in eq 7. Hence, under these conditions one expects a reaction that is first order in A but independent of nucleophile concentration in agreement with the results shown in Table III. The mean values for k_1 are shown in Table VII.

The reaction of $C_5H_5Mo(CO)_2CH_3$ and triphenylphosphine did not go to completion over the range of phosphine concentrations used. The approach to equilibrium was first order in $C_5H_5Mo(CO)_2CH_3$ and the observed rate constant varied with phosphine concentration.

Assuming the direct reaction is negligible (k_5 and k_6 are equal to zero), eq 5 then reduces to a form which may be integrated giving the expression (where $[A_{Eq}]$ represents the concentration of starting material at equilibrium)

$$\ln\left(\frac{[A_0] - [A_{Eq}]}{[A] - [A_{Eq}]}\right) = \frac{k_1k_3[L] + k_4k_2}{k_2 + k_3[L]}t \qquad (8)$$

which predicts an approach to equilibrium which is first order in $C_5H_5Mo(CO)_3CH_3$, in agreement with our results. The observed rate constant may be written as

$$k_{obsd} = k_1\left[\frac{[L] + \frac{k_2k_4}{k_1k_3}}{[L] + \frac{k_2}{k_3}}\right] \qquad (9)$$

It was possible to measure k_4 directly by following the rate of decarbonylation of $C_5H_5Mo(CO)_2(COCH_3)P(C_6H_5)_3$ to $C_5H_5Mo(CO)_3CH_3$ and $P(C_6H_5)_3$. There was no spectral evidence for a decarbonylation reaction to give $C_5H_5Mo(CO)_2CH_3P(C_6H_5)_3$ in a manner similar to that of $CH_3COMn(CO)_4P(C_6H_5)_3$ to give $CH_3Mn(CO)_4P(C_6H_5)_3$. Barnett and Treichel[9] do isolate $C_5H_5Mo(CO)_2CH_3P(C_6H_5)_3$ as the major product and some $C_5H_5Mo(CO)_3CH_3$ on the decarbonylation of $C_5H_5Mo(CO)_2(COCH_3)P(C_6H_5)_3$ in refluxing tetrahydrofuran. Perhaps this is because under these conditions the CO is permitted to escape from the reaction mixture, whereas this did not happen in our closed systems. Perhaps some $C_5H_5Mo(CO)_2CH_3P(C_6H_5)_3$ is also formed in the closed system, but not in sufficient amount to be detected. However, this may be responsible for the differences found between calculated and experimental values for k_{obsd} and for equilibrium constants described next.

Knowing k_1 and k_4 (Table III) it was possible to substitute these in eq 9 and to calculate values of k_2/k_3. The mean value of k_2/k_3 was then used to recalculate k_{obsd} for different phosphine concentrations with satisfactory agreement as shown in Table III. The observed constant should approach k_1 at very large triphenylphosphine concentrations. From direct spectrophotometric observation of the position of equilibrium in several runs, an approximate equilibrium constant was calculated

$$K = \frac{[C_5H_5Mo(CO)_2(COCH_3)(C_6H_5)_3P]}{[C_5H_5Mo(CO)_3CH_3][(C_6H_5)_3P]} \tag{10}$$
$$= 28.2 \pm 6.0 \text{ l./mole}$$

This was in reasonable agreement with the value calculated from the ratio of the rate constants

$$K = \frac{k_1k_3}{k_2k_4} = 19.2 \pm 3.8 \text{ l./mole}$$

Investigations of three reactions in toluene solution differ from observations made in tetrahydrofuran solution. The results in Table IV show that the rates of reaction are dependent on nucleophile concentration. Tri-*n*-butylphosphine and tri-*n*-butyl phosphite follow a mixed-order reaction path (Figure 2) with k_{obsd} given by eq 7.

The values of k_1 and k_5 are given in Table VII. The results with triphenylphosphine and triphenyl phosphite are somewhat unexpected. It appears that pure second-order conditions exist (Figure 2). Referring to mechanism B, if $k_3[L]$ is less than k_2, the solvent path is effectively blocked and the reaction will proceed almost completely by the direct second-order path. Such a situation can be appreciated if the intermediate is not effectively captured by the poor nucleophiles such as triphenylphosphine, whereas it is captured by the better nucleophiles such as tri-*n*-butylphosphine.

Under these conditions eq 5 reduces to

$$-\frac{d[A]}{dt} = k_5[A][L] - k_6[C] \tag{11}$$

The reaction with triphenyl phosphite goes to completion, whereas with triphenylphosphine it approaches equilibrium. Therefore, for triphenyl phosphite and the initial rates with triphenylphosphine, k_6 may be ignored and k_5 determined. The values for k_5 are shown in Table VII.

The rates of reaction of $C_5H_5Mo(CO)_3CH_3$ with triphenyl phosphite in nitromethane shown in Table IV are independent of phosphine concentration. The approximate value of k_1 is given in Table VII. Only one reaction was performed in dimethylformamide (Table IV) and the rate was fast, just within the limits of observation using our method.

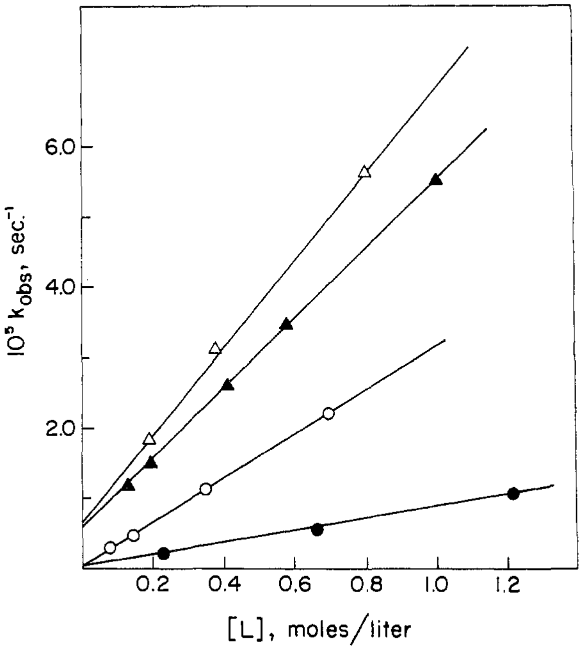


Figure 2.—Plot of the observed rate constants *vs.* nucleophile concentrations for the reaction of $C_5H_5Mo(CO)_3CH_3$ with different reagents in toluene solution at 50.7°: △, $P(n\text{-}C_4H_9)_3$; ▲, $P(n\text{-}OC_4H_9)_3$; ○, $P(C_6H_5)_3$; ●, $P(OC_6H_5)_3$.

Discussion

The reactions of $CH_3Mn(CO)_5$ with phosphines and phosphites in tetrahydrofuran are faster than the corresponding reactions of $C_5H_5Fe(CO)_2CH_3$ and $C_5H_5Mo(CO)_3CH_3$ which proceed by similar mechanisms. Assuming that the acetyl derivatives are formed by methyl migration,[3,5] then the difference in the rates probably parallels the strength of the metal to methyl carbon bonds. This same order of M–C bond strength was observed in that the rate of carbon monoxide exchange with $Mn(CO)_5X$ is faster than with $C_5H_5Fe(CO)_2X$.[17]

The reactions of $C_5H_5Fe(CO)_2CH_3$ are limited to phosphines and phosphites. No reaction took place with cyclohexylamine. Bibler and Wojcicki[6] obtained similar results with other nucleophiles and suggested that since the nucleophiles which do not react are weaker π bonders than phosphines or phosphites, their inability to react may be due to the insufficient π-bonding capacity of the donor atom. This idea was supported by the fact that $C_5H_5Fe(CO)_2CH_3$ undergoes insertion reactions with carbon monoxide[7] and sulfur dioxide,[18] both of which are good π-bonding groups. This explanation may also be invoked for the failure of cyclohexylamine, which cannot π bond, to react.

The values obtained for k_1, the rate of formation of intermediate for the $C_5H_5Fe(CO)_2CH_3$ reactions (Table VI), are in good agreement with one another, adding further support to mechanism A. The values for the ratio k_2/k_3 are also shown in Table VI. The smaller this ratio, the better the reagent competes for the intermediate which means the greater its nucleophilic strength. The results show that this decreases in the

[17] A. Wojcicki and F. Basolo, *J. Am. Chem. Soc.*, **83**, 525 (1961).

[18] J. P. Bibler and A. Wojcicki, *ibid.*, **88**, 4862 (1966).

order $P(n\text{-}C_4H_9)_3 < P(n\text{-}OC_4H_9)_3 < P(C_6H_5)_3$ which is in accord with previous correlation of nucleophilicity toward substrates of this type.[15,19]

Bibler and Wojcicki[6] noted the great effect of solvent on the reaction of $C_5H_5Fe(CO)_2CH_3$ with $P(C_6H_5)_3$. Under similar conditions of time and temperature the formation of $C_5H_5FeCO(COCH_3)P(C_6H_5)_3$ is complete in tetrahydrofuran solution, whereas no detectable reaction takes place in hexane solution. Such a result is consistent with mechanism A in which the coordinating solvent can provide a path for reaction. The position of attack by the solvent to generate the active intermediate remains ambiguous. Attack is generally assumed to take place at the metal, but it is also known[20] that hard bases do attack the carbonyl carbon in metal carbonyls.

The results for $C_5H_5Mo(CO)_3CH_3$ show that the solvent also plays an important part in the reactions. Reference to Table V shows that k_1, the rate of formation of the intermediate, varies over a range of greater than four orders of magnitude in changing the solvent from toluene to dimethylformamide. The values of k_1 in tetrahydrofuran are in good agreement with each other as are those in toluene.

The results also indicate that the nature of the entering nucleophile is important, first, in effecting the formation of the acetyl derivatives, and second, in the effect on the mechanism. Iodide ion reacts[4a] with $CH_3Mn(CO)_5$ to form the acetyl ion $[CH_3COMn(CO)_4I]^-$. However, no reaction occurs between $C_5H_5Mo(CO)_3CH_3$ and iodide ion in tetrahydrofuran over a period of 1 week.

The resultant mechanism for any of the reactions of $C_5H_5Mo(CO)_3CH_3$ seems to depend upon the interplay of the coordinating ability of the solvent and the nucleophilicity of the ligand. The reactions of $C_5H_5Mo(CO)_3CH_3$ are extremely sensitive to changes in either solvent or nucleophile. Reference to Table V shows that the rates of reaction of $C_5H_5Mo(CO)_3CH_3$ only become dependent on nucleophile concentration when either the nucleophilicity of the nucleophile is very high or the coordinating power of the solvent is extremely low, or both.

The values of k_5 in toluene (Table VII) are a measure of how good the nucleophile is. The series $P(n\text{-}C_4H_9)_3 > P(n\text{-}OCH_4H_9)_3 > P(C_6H_5)_3 > P(OC_6H_5)_3$ is the customarily observed one.[15,18]

In summary, the reactions of $C_5H_5Fe(CO)_2CH_3$ and of $C_5H_5Mo(CO)_3CH_3$ with various reagents and in different solvents appear to proceed by a solvent- and/or nucleophile-assisted methyl migration onto an adjacent carbonyl carbon. The activation parameters for the tetrahydrofuran-assisted reactions of these two substrates are compared with the values reported earlier for the corresponding reaction of $CH_3Mn(CO)_5$ (Table V). The entropy of activation is responsible for the reaction of molybdenum being slower than that of manganese, whereas the enthalpy term causes the reaction of the iron compound to be the slowest. This suggests a possible $M-CH_3$ bond strength order for different metals of $Fe > Mo \sim Mn$.

The infrared spectra (Table I) of the acetyl derivatives, $C_5H_5Mo(CO)_2(COCH_3)L$, are very similar. Three strong carbonyl stretching absorptions are observed, two terminal ones (the absorption at lower frequency is the more intense) and an acetyl one. All of the frequencies are lower than those observed[8] for the parent compound $C_5H_5Mo(CO)_3COC_2H_5$. In a benzene solution of the latter, the terminal CO groups absorb[11] at 2016 and 1930 cm^{-1}, and the acetyl absorbs at 1675 cm^{-1}. The replacement of CO by the more basic phosphines and phosphites enhances π bonding between the metal and the remaining terminal and acetyl carbonyl groups. This results in a reduction of the carbon-oxygen bond orders of both the terminal and the acetyl CO groups and hence a lowering in the CO stretching frequencies. For the series of compounds $C_5H_5Mo(CO)_2(COCH_3)L$, the lowest frequencies are found for $L = P(n\text{-}C_4H_9)_3$, which agrees with its being the strongest base and poorest π bonder of the ligands used. The acetyl CO stretching frequency found for $C_5H_5Mo(CO)_2(COCH_3)P(C_6H_5)_3$ shows an appreciable solvent dependence (Table I) and this should be further investigated.

Acknowledgment.—This research was supported in part by National Science Foundation Grant GP-5479X.

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