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RATE-STRUCTURE STUDIES OF THE CARBONYLATION AND DECARBONYLATION OF SUBSTITUTED METAL CARBONYL COMPLEXES *

J N CAWSE R A FIATO and R L PRUETT **

Union Carbide Corporation, Chemicals and Plastics, South Charleston, West Virginia 25303 (U S A)

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Summary

The rate of CO insertion for the following complexes have been determined $RCH_2Mn(CO)_5$ where R = cyclohexyl, hydrogen, phenyl, methoxy, and carboxyl, $RCH_2Fe(CO)_4^-$ where R = cyclohexyl, n-octyl, n-heptyl, and phenyl It appears that a Taft σ—ρ correlation can be established for this reaction Rate data for the decarbonylation reaction of an analogous series of substituted manganese carbonyl complexes ($RCH_2COMn(CO)_5$) was also obtained As in the case of the CO insertion reaction, the rates increase as the Taft σ for RCH_2 decreases

The linear free energy relationships (LFER) generated in this study have been used to predict the relative probability of several reaction steps that have been postulated for the conversion of carbon monoxide and hydrogen into ethylene glycol

Introduction

A basic step in the overall reaction sequence inherent in the conversion of carbon monoxide and hydrogen (synthesis gas) to industrial chemicals is the reversible carbonylation of metal carbonyl complexes

$$RM(CO)_n \underset{-CO}{\overset{+CO}{\rightleftharpoons}} RCOM(CO)_n$$

(R = H, alkyl, aryl)

While a number of studies have been conducted to elucidate the mechanism of this interconversion, only a few [1—3] have been concerned with establish-

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* Presented in part at the 9th Regional Amer Chem Soc Meeting Charleston W Va October 1977

** Present address Exxon Research and Engineering Co P O Box 45, Linden N J 07036 (U S A) ing a comprehensive rate-structure relationship The preliminary nature of that work, however, has left many questions unanswered and has given rise to several dissimilar theories regarding the rate-controlling features of this sequence

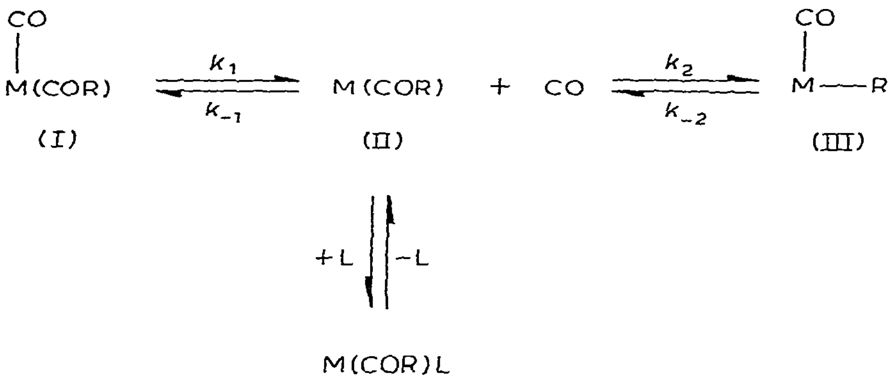
In order to resolve these problems we have attempted to supplement the data presented in previous reports by conducting rate-structure studies of the carbonylation and decarbonylation of a variety of substituted metal (M = Mn, Fe) carbonyl complexes We now wish to report the results of that study

Results and discussion

Part I

Studies designed to elucidate the mechanism of the interconversion of alkyl- and acyl-metal carbonyl complexes have attracted much attention [1,2] A simplified mechanistic representation of this carbonylation-decarbonylation sequence is presented in Scheme 1

SCHEME 1



In the overall conversion of I to III, the first step, I → II, has been postulated [1] to be rate determining when M = Mn. It should be noted, however, that in the case of acyliridium [3] complexes (e g. $IrCl_2(PPh_3)_2COCH_2Ph$) the conversion of II to III appears to be a slow process.

We have attempted to supplement the data persented in previous studies [4] by determining the decarbonylation rates for the complexes, $RCOMn(CO)_5$, listed in Table 1

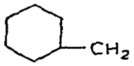
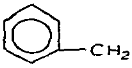
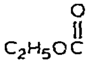
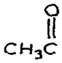
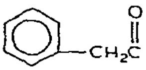
Previous data, as well as that obtained in this study, indicates that the experimentally observed rate laws for the conversion of I to III conform to eq 1 [1,2] In addition, it has been generally accepted that k_{obs} can most accurately be

$$\frac{d[I]}{dt} = k_{obs}[I] \qquad (1)$$

ascribed to k_1 when M = Mn [1,2] Implicit in this interpretation [1b] is the fact that those factors which accelerate CO dissociation should also accelerate the rate of conversion of I to III Furthermore, within a given series of mono-substituted manganese carbonyl complexes it appears that CO dissociation is favored in those complexes whose pendant substituents can most effectively

TABLE 1

DECARBONYLATION RATES FOR RC(=O)Mn(CO)$_5$ AT 80°C IN BENZENE

	Complex	$10^5 k$ (sec^{-1}) at 80 °C
R =		$\gtrsim$ 250 ±20
R =	CH_3	250 ±15 (290) [4]
R =		159 ±12 0
R =	CH_3OCH_2	58 ±4 5
R =	 $C_2H_5OC(=O)$	28 ±3 1
R =	 $CH_3C(=O)$	(21) [4]
R =		(20) [4]
R =	CF_3	2 8 ±0 9

withdraw electron density from the metal center [1b] *. Hence the conversion of I to III should be accelerated by incresed electron-withdrawing ability of the substituent (RCO) group in I

The data in Table 1 suggest that this is not the case The complexes are arranged in order of increasing electron-withdrawing ability of the RCO substituent (estimated [6] from the Taft σ^* of the R in RCO). The rates of decarbonylation decrease in the same order (i e as σ^* R increases)

This observation could be rationalized by assuming that the second step II → III is also kinetically significant If [CO] $k_{-1} \approx k_2$ [1a] and k_{-2} is not significant then the rate law could be expressed as in eq 2

$$\frac{d[I]}{dt} = k_{obs}[I] = \frac{k_1 k_2 [I]}{k_{-1}[CO]} \tag{2}$$

While the first-order rate dependence on [I] is retained, this treatment also predicts that CO inhibition should be observed A further consequence of this treatment is that the rate of decarbonylation, d[MR]/dt, should be less than the rate of substitution, d[M(COR)L]dt, see Scheme 1 In actual practice, however, Wojcicki has noted that this condition is not strictly fulfilled and d[M(COR)L]/d$t \approx$ d[MR]/dt [1a]

The apparent dilemma can be resolved by comparison of the present data to that which was provided by Heck [7] in rate-structure studies of the follow-

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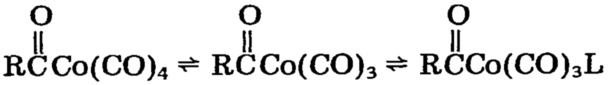
[*] The basic theory suggests that a reduction in electron density reduces the amount of M—CO back-bonding which results in more facile CO dissociation

ing reaction



$$RC(=O)Co(CO)_4 \rightleftharpoons RC(=O)Co(CO)_3 \rightleftharpoons RC(=O)Co(CO)_3L$$

In that study the rate of formation of the coordinatively unsaturated species, $RCOCo(CO)_3$, decreased as the electron-withdrawing ability of RCO increased The origin of this rate reduction, which is in apparent disagreement with that previously proposed for manganese [1b,5], was that as a substituent caused electron density to be removed from the metal center the loss of two more electrons with the departing ligand (CO) would be unfavorable

If this theory is applied to the data in Table 1 we can then accommodate a k_1 rate-determining step as well as the reduction in rate with increased electron withdrawing ability of (RCO). In addition, we see that the substituent effects in the manganese system are ca 10-fold greater than those observed with cobalt At present we do not wish to speculate as to the origin of this effect other than to note that the absolute decarbonylation rates are higher for the acylcobalt system

Part II

Determination of the relative rates of carbonylation of a series of substituted methylmanganese and -iron complexes (Scheme 2) shows that a linear free

SCHEME 2

$$RCH_2Mn(CO)_5 + CO \rightarrow RCH_2COMn(CO)_5$$

$$RCH_2Fe(CO)_4^- + PPh_3 \rightarrow RCH_2COFe(CO)_3(PPh_3)^-$$

energy relationship (LFER) (Taft $\sigma^* - \rho^*$) can be established for these reactions The susceptibility of these carbonylation reactions to polar effects is very large

Numerous studies of alkylmetal carbonyls and their reactions have shown that carbonyl insertion becomes more difficult as the electron-withdrawing ability of the substituent increases

System	Rates noted	Reference
$CpFe(CO)_2R$	i-Pr > Et > Me	8
$CpMo(CO)_3R$	Et > Me > CH_2Ph > $CH_2CH{=}CH_2$	9 10
$RMn(CO)_5$	n-Pr > Et > Ph > Me	11
$RCo(CO)_4$	$PhCH_2$ < "other alkyls"	12

No efforts to correlate this effect via a LFER have appeared in the literature.

In this work the rates of a series of substituted methyl substituents on iron carbonyl anion and manganese carbonyl complexes were evaluated Use of a common CH_2 attachment to the metal center yielded a good LFER correlation over a reasonable range of substituents The two different metal complexes allow comparison of the effects across differences in metal atom, oxidation state, charge, and *d*-electron configuration

Complex	Metal	Oxidation state	Charge on complex	d-Electron configuration
$RFe(CO)_4^-$	Fe	0	—1	d^8
$RMn(CO)_5$	Mn	+1	0	d^6

The rates of the carbonylations are given in Tables 2 and 3, and are plotted as log k vs σ^* (Fig 1)

It is clear from Fig 1 that the two systems show large, similar effects of polar substituents on the carbonyl insertion reaction Over the σ^* range from —0.13 to +0.215 the effect is nearly linear, despite substituents chosen for significant steric (cyclohexylmethyl) and resonance (benzyl) contributions The reaction constant ρ^* is the same within experimental error (—8 8 and —8 7) for the two systems

As σ^* increases beyond +2 15 the points no longer fit the line This may be indication of a change in mechanism, but also may be caused by the difficulties of accurate measurements of such sluggish reactions

This very large negative ρ^* dramatizes the effect of electron-withdrawing groups in slowing the reaction A simplified mechanism of this reaction can be written (Scheme 3) [1] When the concentration of L is low and k_{-2} is appreciable, an acceptable approximation for these systems [1,14] is then

SCHEME 3

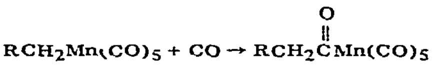
$$\underset{(IV)}{RM(CO)} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \underset{(V)}{RCOM} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \underset{(VI)}{RCOML}$$

$$\frac{-d[RM(CO)]}{dt} = k_{obs}[L][RM(CO)] = \frac{k_4 k_5}{k_{-4}}[L][RM(CO)]$$

An electron-withdrawing group R will clearly have its greatest effect on the

TABLE 2

RATES OF CARBONYLATION FOR A SERIES OF SUBSTITUTED METHYLMANGANESE PENTACARBONYL COMPLEXES AT 30°C IN $\beta\beta$-DIETHOXYDIETHYL ETHER



$$RCH_2Mn(CO)_5 + CO \rightarrow RCH_2\overset{\overset{O}{\|}}{C}Mn(CO)_5$$

R	$\sigma^*(RCH_2)$	$10^5\,k$ (l mol^{-1} sec^{-1})
C_2H_5	—0 115	(14000) [1d]
CH_3	—0 10	(12000) [1d]
cyclo-C_6H_{11}	—0 06	~2500 ± 300 (900) [1d]
H	0 00	1200 ± 190
CH_3O	+0 52	~25 ± 4 0
C_6H_5	+0 22	12 ± 2 5
$HO\overset{\overset{O}{\|}}{C}$	+1 05	⩽5 ± 3 0

TABLE 3

RATES OF CARBONYLATION FOR A SERIES OF SUBSTITUTED METHYLIRON TETRACARBONYL COMPLEXES AT 25°C IN TETRAHYDROFURAN

$$RCH_2Fe(CO)_4^- + PPh_3 \rightarrow RCH_2\overset{O}{\overset{\|}{C}}Fe(CO)_3(PPh_3)$$

R	σ^* (R—CH$_2$)	$10^5\,k$ (mol^{-1} sec^{-1})
n-Octyl	—0 13	(6500) [13]
n-Heptyl [a]	—0 13	4000 ± 300
cyclo-C_6H_{11}	—0 06	150 0 ± 11 5
C_6H_5	+0 22	4 25 ± 2 1

[a] These new compounds were prepared in situ and characterized by examination of their decomposition products the aldehydes and alkanes obtained were compared to authentic materials

first step in this mechanism, the equilibrium ($K = k_4/k_{-4}$) between IV and V

Increasing electron-withdrawing ability in R would be expected to stabilize both alkyl—metal and acyl—metal bonds, but the effect should be greater for the alkyl [14]. The large negative value of ρ^* (—8 7) suggests that in these systems, an increase in σ^* of 0 1 (such as between ethyl and methyl) will result in 0.5 kcal/mol greater stabilization of the alkyl

It is remarkable that the observed ρ^*'s are so similar in two systems differing in metal, oxidation state, charge, and *d*-electron configuration If we assume that a large and negative ρ^* is a common feature of carbonyl insertion reactions, then we can begin to speculate on a number of interesting compounds and reactions

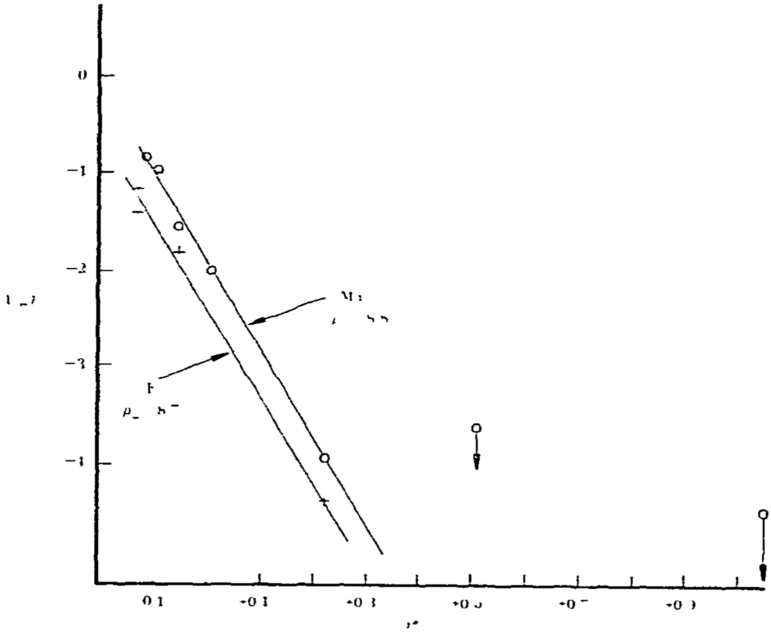
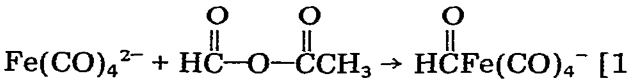
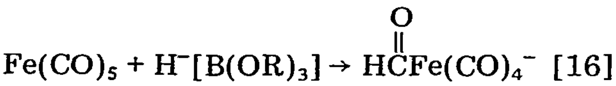


Fig 1 Log *k* vs σ^* for CO insertion reactions

The generation of a formyl complex [15,16] has been implicated as a possible first step in the conversion of synthesis gas into methanol, ethylene glycol and glycerine [17,18]. Although formyl-transition metal complexes are known; they have only been synthesized indirectly.



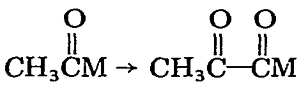
$$\mathrm{Fe(CO)_4^{2-} + H\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}CH_3 \rightarrow H\overset{O}{\overset{\|}{C}}Fe(CO)_4^-}\ [15]$$



$$\mathrm{Fe(CO)_5 + H^-[B(OR)_3] \rightarrow H\overset{O}{\overset{\|}{C}}Fe(CO)_4^-}\ [16]$$

rather than by carbonyl insertion into a metal hydride. We can readily accommodate this situation in light of the large polar substituent effects that were noted above. The σ^* of H is +0.5, and given a large negative ρ^*, one would expect formyl formation from a hydride complex to be very slow [18].

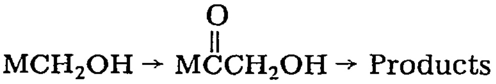
Casey has shown that the interconversion of an acyl complex to the corresponding pyruvoyl complex via carbonyl insertion is a highly disfavored process [4]. Since σ^* for $\mathrm{CH_3CO}$ is +1.65, one might even expect this process



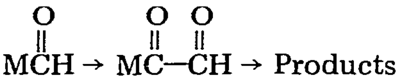
$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}M \rightarrow CH_3\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}M}$$

to be even less favorable than the analogous hydride to formyl interconversion.

Finally, carbon—carbon bond formation in the synthesis of ethylene glycol from carbon monoxide and hydrogen could conceivably occur by two major pathways a and b.



$$\mathrm{MCH_2OH \rightarrow M\overset{O}{\overset{\|}{C}}CH_2OH \rightarrow Products} \qquad \text{(a)}$$



$$\mathrm{M\overset{O}{\overset{\|}{C}}H \rightarrow M\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}H \rightarrow Products} \qquad \text{(b)}$$

In a the CO insertion is effectively into a M—$\mathrm{CH_2OH}$ bond (σ^* +0.55), while in b the insertion is into a M—CHO bond (σ^* +1.5). Given a large negative ρ^*, reaction b would be much slower than reaction a. In addition, a is also likely to be an inherently slow reaction when compared to any similar system in which R is a simple alkyl group.

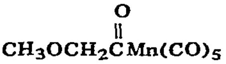
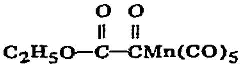
Studies on the preparation and evalution of the chemical behavior of complexes such as $\mathrm{HCOMn(CO)_{5-n}L_n}$, $\mathrm{HOCH_2Mn(CO)_{5-n}L_n}$ and $\mathrm{HOCH_2COMn(CO)_{5-n}L_n}$ are now in progress.

Experimental

General. The manganese [1b] and iron [13] complexes used in this study were prepared by the previously described general procedure involving the reaction of an alkyl or acyl halide with the appropriate lithium or sodium polycarbonyl metallate. Reagent grade solvents used in kinetic studies were

TABLE 4

ANALYTICAL DATA FOR NEW COMPOUNDS

Compound [a]	IR (solvent, cm^{-1})	^{1}H NMR (solvent, σ)	Analysis (found (calcd) (%))	
			C	H
$CH_3OCH_2Mn(CO)_5$	C_6H_6 2125m, 2060(sh) 2005s, 1990(sh)	C_6H_6 3 95 (2 H S) 3 20 (3 H S)	35 43 (35 02)	2 52 (2 09)
 $CH_3OCH_2\overset{\overset{O}{\|}}{C}Mn(CO)_5$	C_6H_6, 2130m 2010vs, 1645m	C_6H_6 3 42 (2 H, S), 3 10 (3 H S)	35 89 (35 84)	2 01 (1 87)
 $C_2H_5O-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}Mn(CO)_5$	CCl_4 2130m, 2020vs 2015(sh) 1730m, 1650m	CCl_4, 4 25 (2 H, q) 1 35 (3 H, t)	36 71 (36 50)	1 66 (1 69)

[a] Sharp melting ranges were not observed for these compounds, instead they exhibited broad decomposition ranges ca. 45—85°C

freshly distilled and degassed before use. The decarbonylation and carbonylation studies were conducted under argon and carbon monoxide, respectively NMR studies were conducted on a Varian A60 or Perkin—Elmer R12B spectrometer. IR studies were conducted on a Beckman IR-12 or Perkin—Elmer 283 spectrometer Elemental analysis (Table 4) were conducted by Schwarzkopf Microanalytical Laboratories, Woodside, New York,

Kinetics. A procedure similar to that described by Casey [4] was employed for all kinetic runs. Reaction solutions were charged to a Fisher—Porter bottle which was purged with the appropriate gas After taking a time = 0 aliquot the system was placed in an oil bath equipped with a thermostatic controller (T ±0.5°C)

Samples were withdrawn through a dip tube and immediately analyzed by NMR and IR The runs were each repeated at least three times and the rate data presented in Tables 1, 2 and 3 represent the average of these determinations

In a test of this procedure it was shown that decarbonylation rate data for $CH_3COMn(CO)_5$ was in good agreement with that reported by Casey, see Table 1

Error limits are presented as standard deviation of the mean value at the 95 percent confidence level.

Acknowledgements

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