Volume 10
Number 10
October 1971

Inorganic Chemistry

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Kinetics and Mechanism of the Cleavage Reactions of Acylmanganese Pentacarbonyl and Methylmanganese Pentacarbonyl

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Received March 9, 1971

We have investigated the reactions of acylmetal compounds, particularly $CH_3COMn(CO)_5$, with a variety of nucleophiles. The rates and kinetic patterns show that $CH_3COMn(CO)_5$ behaves much like an amide. Furthermore, the kinetic behavior of the acid-catalyzed solvolysis of $CH_3COMn(CO)_5$ resembles that of an amide. We have also examined the reaction of $CH_3Mn(CO)_5$ with HCl in methanol to form methane and $ClMn(CO)_5$. The rate is dependent on the acid concentration and is significantly increased by additions of KCl. $HgCl_2$ is superior to HCl as a cleaving agent and $Hg(OAc)_2$ is better still.

Introduction

Strong bases are known to react with acylmetal complexes to displace the metal and form a new acyl derivative. Heck and Breslow[1] have shown that, in the presence of base, alcohols react rapidly with acylcobalt tetracarbonyls to form esters (eq 1). Keblys and Fil-

$$RCOCo(CO)_4 + R'O^- \longrightarrow RCO_2R' + Co(CO)_4^- \quad (1)$$

bey[2] have also observed cleavage of acylmanganese complexes by OH^- and OCH_3^-.

With many nucleophiles, however, the acyl group is not affected. Instead, 1 mol of CO is slowly evolved and the nucleophile is bound to the metal. Reaction 2 has been studied for L = $P(C_6H_5)_3$,[3,4] $NH_2C_6H_{11}$,[2a,5]

$$CH_3COMn(CO)_5 + L \longrightarrow CH_3COMn(CO)_4L + CO \quad (2)$$

$NH_2C_4H_5$,[5] and I^-.[5,6] The rates are independent of the nature and concentration of L. The reaction of $CH_3{}^{13}COMn(CO)_5$ with $P(C_6H_5)_3$ leads to retention of the ^{13}C label in the acetyl position. Clearly the mechanism in these cases involves a simple dissociative loss of a CO ligand. Heck[7] has studied similar reactions of acylcobalt carbonyls with $P(C_6H_5)_3$.

There are at least two possible sites for the reaction of acylmetal carbonyls with nucleophiles—the acyl carbonyl or the metal. We have investigated the reactions of acyl complexes, particularly $CH_3COMn(CO)_5$, with a variety of nucleophiles to determine which will attack the carbonyl and which will attack the metal. The reactions involving cleavage of the carbon–metal bond have been studied kinetically to demonstrate the relationship between $CH_3COMn(CO)_5$ and organic carboxylic acid derivatives.

In alkylmetal complexes, the high electronegativity of a carbon atom relative to a metal leads to polarization of the carbon–metal bond in the direction $C^{\delta-}$–$M^{\delta+}$. Thus, the carbon atom is susceptible to attack by *electrophiles.* The major part of the information concerning cleavage of alkylmetal bonds comes from the extensive studies on the compounds of the main-group metals. The results have been discussed in several reviews.[8–11] Many electrophilic centers exist with attached nucleophilic groups. Attack by such a reagent may involve a strong nucleophilic interaction with the metal as well as an electrophilic interaction at carbon. Although no unambiguous proof is available, most authors favor such a four-center mechanism for the organometallic derivatives of groups IIb and IVa.

Different behavior has been observed for the acid cleavage of transition metal alkyls. Cleavage of benzylchromium(III) ion involves initial nucleophilic substitution on the metal.[12] In methylplatinum(II) complexes, oxidative addition of HCl to the metal gives a platinum(IV) hydride intermediate which then loses methane.[13] With the pentacyanoalkylcobalt(III) complexes, electrophilic attack does not occur on the alkyl group or the metal but on the cyanide ligand; alkyl migration then gives the intermediate which leads to the nitrile products.[14] $CH_3Mn(CO)_5$ is known to react with strong acids to form methane,[15] but mechanistic

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(1) (a) R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, **85**, 2779 (1963); (b) R. F. Heck, *Advan. Organometal. Chem.*, **4**, 243 (1966); (c) R. F. Heck, *J. Amer. Chem. Soc.*, **85**, 1460 (1963).

(2) (a) K. A. Keblys and A. H. Filbey, *ibid.*, **82**, 4204 (1960); (b) K. A. Keblys, U. S. Patents 3,081,324 (1963) and 3,081,338 (1963); *Chem. Abstr.*, **59**, 6439 (1963).

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studies on this neutral, coordinatively saturated derivative have not been reported previously.

Experimental Section

Preparation and Purification of Materials.—All solvents were distilled under nitrogen. Tetrahydrofuran was refluxed over LiAlH$_4$. Methanol was purified by published procedures.[16] Saturated hydrocarbon solvents were refluxed over sodium wire and distilled. Dichloroethane was distilled from phosphorus pentoxide.

Compounds obtained from commercial sources as reagent grade materials were used without further purification. Cyclohexylamine was distilled *in vacuo*. Hydroxylamine[17] and anhydrous hydrogen chloride[18] were prepared by published procedures. The monohydrate of *p*-toluenesulfonic acid was dried by heating at 40° under vacuum for 3 hr.

All the organometallic complexes used in this study are well-known compounds which were prepared by literature procedures: CH$_3$COMn(CO)$_5$,[19] CH$_3$COCo(CO)$_4$,[20] CH$_3$COCo(CO)$_3$(P(C$_6$H$_5$)$_3$),[20] CF$_3$COMn(CO)$_5$,[21] and CH$_3$Mn(CO)$_5$.[22]

Identification of Products.—In most reactions involving cleavage of the acetyl–metal bond, the products could be easily identified by the infrared spectrum. The reaction of CH$_3$COMn(CO)$_5$ with NaOCH$_3$ in methanol gave Mn(CO)$_5^-$ and methyl acetate (1745 and 1730 cm^{-1}). Further evidence for methyl acetate was obtained by distillation of the methanol–methyl acetate azeotrope. The reaction with CH$_3$COCo(CO)$_4$ and CH$_3$COCo(CO)$_3$(P(C$_6$H$_5$)$_3$) gave methyl acetate and the carbonyl anions Co(CO)$_4^-$ (1900 cm^{-1}) and Co(CO)$_3$(P(C$_6$H$_5$)$_3$)$^-$ (1860 cm^{-1}). The phosphine-substituted anion decomposed rapidly to give some Co(CO)$_4^-$. CF$_3$COMn(CO)$_5$ and NaOCH$_3$ initially gave CF$_3$CO$_2$CH$_3$, identified by its CO stretch at 1790 cm^{-1}. Due to the presence of a small amount of water, the final product was CF$_3$CO$_2$Na (1680 cm^{-1}).

Anhydrous HCl was bubbled through a solution of CH$_3$COMn(CO)$_5$ in methanol for 5 min and then neutralized. The infrared spectrum showed conversion to NaMn(CO)$_5$ and CH$_3$CO$_2$CH$_3$. Similarly, *p*-toluenesulfonic acid showed smooth conversion to methyl acetate (1745, 1730 cm^{-1}) and HMn(CO)$_5$ with its characteristic bond at 2010 cm^{-1}.

Other nucleophiles do not react at all with CH$_3$COMn(CO)$_5$ or react only slowly to give the CO-substitution product. Such reactions have already been reported for L = P(C$_6$H$_5$)$_3$, NH$_2$C$_6$H$_{11}$, NH$_2$C$_4$H$_9$, and I$^-$. Our studies in methanol show similar results with F$^-$, CH$_3$CO$_2^-$, NO$_3^-$, NH$_3$, and pyridine. For reactions in aqueous solution, phosphate buffers were used to maintain neutral pH. Under these conditions, no reaction occurred with CH$_3$COMn(CO)$_5$. Therefore HPO$_4^{2-}$ and H$_2$PO$_4^-$ do not attack the acyl carbonyl. Imidazole also had no effect on the hydrolysis of CH$_3$COMn(CO)$_5$. The proposed anionic complexes from F$^-$, CH$_3$CO$_2^-$, and NO$_3^-$ were too unstable to isolate, but the infrared spectral changes and CO evolution data are similar to the results for I$^-$.[5]

The cleavage of CH$_3$Mn(CO)$_5$ with HCl in methanol gave methane which was measured by gas evolution. The inorganic product was unstable under the conditions of the experiments. However, when the reaction was carried out in dichloroethane, the product was shown to be ClMn(CO)$_5$ by the absorption band which appeared at 377 nm. Similarly, HgCl$_2$ in dichloroethane gave ClMn(CO)$_5$ with infrared bands at 2142, 2059, and 2006 cm^{-1}. Removal of solvent and sublimation of the residue gave a white solid with infrared and nmr spectra identical with those of CH$_3$HgCl. In methanol, the initial spectral changes were the same, but as noted before, the ClMn(CO)$_5$ was unstable.

Determination of Rates.—The reactions were usually followed by observing the decrease of absorbance of the organometallic complex in the 220–300-nm range. Pseudo-first-order conditions were maintained by using a large excess of the electrophilic or nucleophilic reagent. A Cary 14 spectrophotometer was used for preliminary runs, but most of the data were collected using a Beckman DU spectrophotometer.

In some cases, rates were measured by following the decrease of carbonyl bands in the infrared spectrum using a Perkin-Elmer Model 337 spectrophotometer. The band followed had to be well separated from bands due to other species since the resolution obtainable in methanol is poor. CaF$_2$ cells were used in these experiments.

Results

Cleavage of CH$_3$CoMn(CO)$_5$.—Nucleophiles can react at two distinctly different sites of acylmetal carbonyls, as shown by eq 1 and 2. The results of this study show that only the most reactive nucleophiles will attack the acyl carbonyl. In fact only OCH$_3^-$, OH$^-$, and the abnormally reactive hydroxylamine have been observed to be effective reagents in the cleavage of the acetyl group in CH$_3$COMn(CO)$_5$.

The reaction with methoxide ion in methanol to give methyl acetate and manganese pentacarbonyl anion is first order in each reagent as shown in Table I. The second-order rate constant is 0.11 M^{-1} sec^{-1} at 25°. The alkaline hydrolysis of CH$_3$COMn(CO)$_5$ proceeds according to eq 3. It is clear from the data in Table I that the rate is more than first order in hydroxide ion concentration. The reaction follows the rate law

TABLE I
REACTION OF CH$_3$COMn(CO)$_5$ WITH SEVERAL NUCLEOPHILES AT 25°

Nucleophile	Nucleophile concn, 10^2[N], M	10^4k_{obsd}, sec^{-1}	k_{obsd}/[N], M^{-1} sec^{-1}
NaOCH$_3$ in methanol	0.078	0.90	0.11
	0.288	2.92	0.10
	0.610	6.72	0.11
	0.900	11.1	0.12
	0.600[a]	. . .	0.11
NaOH in water	0.425	5.25	0.124
	0.850	21.2	0.250
	1.275	45.4	0.356
	1.70	75.0	0.441
NH$_2$OH in water	1.10[b]	0.90	0.0082
	2.96	2.03	0.0069
	3.08	1.87	0.0061
	4.32	2.53	0.0059
	5.42	3.54	0.0065

[a] Measured by infrared spectroscopy using second-order conditions, *i.e.*, [NaOCH$_3$]$_0$ = [CH$_3$COMn(CO)$_5$]$_0$. [b] Free hydroxylamine concentration calculated from total hydroxylamine concentration, pH, and pK_a(NH$_3$OH$^+$) = 6.20.

$$\mathrm{CH_3COMn(CO)_5 + 2NaOH \longrightarrow CH_3CO_2Na + NaMn(CO)_5 + H_2O} \quad (3)$$

$$\text{rate} = \{k_2[\mathrm{OH^-}] + k_3[\mathrm{OH^-}]^2\}[\mathrm{CH_3COMn(CO)_5}] \quad (4)$$

$$k_{\text{obsd}} = k_2[\mathrm{OH^-}] + k_3[\mathrm{OH^-}]^2$$

A plot of $k_{\text{obsd}}/[\mathrm{OH^-}]$ *vs.* [OH$^-$] was linear with an intercept (k_2) of 0.025 M^{-1} sec^{-1} and a slope (k_3) of 24.9 M^{-2} sec^{-1} at 25°.

The data for the reaction with hydroxylamine are also reported in Table I. Products could not be isolated due to the low concentrations required by the limited solubility of CH$_3$COMn(CO)$_5$ in water. However, the FeCl$_3$ test[23] for hydroxamic acid (CH$_3$CONHOH) was negative and the changes in the electronic spectrum were identical with the changes observed during alkaline hydrolysis. Therefore, the reaction with NH$_2$OH involves either nucleophilic

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[22] M. H. Abraham and J. A. Hill, *J. Organometal. Chem.*, **7**, 147 (1967).

[23] W. P. Jencks, *J. Amer. Chem. Soc.*, **80**, 4581 (1958).

catalysis or general base catalysis of the hydrolysis of $CH_3COMn(CO)_5$. These reactions were studied in solutions buffered to keep pH between 6.3 and 6.5. Small errors in pH measurement led to relatively large errors in the calculated concentration of free hydroxylamine since the computation involved the difference between pH and the pK_a of NH_3OH^+ (6.20). However, it is clear that the reaction is first order in each reagent with $k_2 \simeq 6.4 \times 10^{-3}\ M^{-1}\ sec^{-1}$ at 25°.

Acid-Catalyzed Solvolysis.—The reaction of CH_3CO-$Mn(CO)_5$ with methanol is catalyzed by acids. The data are shown in Figure 1. The rate increases with acid concentration but approaches a rate maximum above 0.1 *M* acid. This is the behavior expected for a rapid preequilibrium to form a protonated intermediate which then reacts with solvent in the rate-limiting step. Evidence for such an intermediate was obtained by following the intensity of the acetyl CO stretching bond, which gives a direct measure of the concentration of $CH_3COMn(CO)_5$. The acetyl stretch cannot be observed in methanol due to solvent interference. With an acid concentration of 0.1 *M* in 5% methanol–dioxane, the intensity decreased immediately by about 15% as the equilibrium was established and then decreased at a slower rate as the intermediate reacted with solvent.

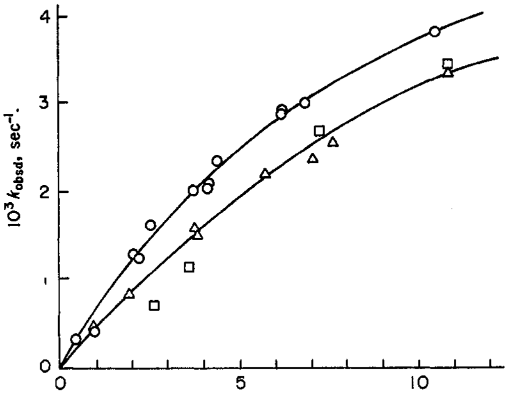


Figure 1.—Plot of observed rate constant *vs.* [H^+] for acid-catalyzed solvolysis of $CH_3COMn(CO)_5$ in methanol: ○, hydrochloric acid; □, perchloric acid; △, *p*-toluenesulfonic acid.

Addition of small amounts of water markedly slowed down the rate of acid-catalyzed solvolysis. In water as a solvent, even 2 *M* HCl produces no increase in rate over that of the solvolytic cleavage. This effect is presumably related to the weaker acid strength of H_3O^+ compared to that of $CH_3OH_2^+$. The higher rates of cleavage with HCl indicated in Figure 1 is probably related to a more anhydrous environment with this acid.

Base Cleavage of Other Acyl Compounds.—The rates of reactions of other acylmetal derivatives with sodium methoxide were investigated. $CH_3COCo(CO)_4$ was cleaved by 0.05 *M* $NaOCH_3$ in less than 2 min. $CH_3COCo(CO)_3(P(C_6H_5)_3)$ reacted at 25° with a second-order rate constant of $1.0 \times 10^{-2}\ M^{-1}\ sec^{-1}$. $CH_3CH_2CH(CH_3)COFe(CO)(P(C_6H_5)_3)(C_5H_5)$[24] reacted extremely slowly even in concentrated alkaline solution. These results demonstrate the following leaving-group effect

$$Co(CO)_4^- \gg Mn(CO)_5^- > Co(CO)_3(P(C_6H_5)_3)^- \gg Fe(CO)(P(C_6H_5)_3)(C_5H_5)^- \qquad (5)$$

Trifluoroacetylmanganese pentacarbonyl was prepared to investigate the effect of electron-withdrawing groups in the acyl moiety. The reaction with $NaOCH_3$ is much faster than with the acetyl compound.

$$CF_3COMn(CO)_5 \gg CH_3COMn(CO)_5 \qquad (6)$$

Cleavage of $CH_3Mn(CO)_5$.—$CH_3Mn(CO)_5$ is readily cleaved by HCl in methanol to form methane and $ClMn(CO)_5$. As shown in Table II, the rate is proportional to the acid concentration. Addition of NaCl at constant ionic strength caused a significant rate increase. Figure 2 shows the remarkable decrease in rate as water is added to the system. Other protic acids were investigated. $HClO_4$ gave only a barely detectable increase in the rate of uncatalyzed solvolysis. With the very weak acid CH_3CO_2H, no catalysis was observed.

Table II

Cleavage of $CH_3Mn(CO)_5$ by HCl in Methanol at 25°
($[CH_3Mn(CO)_5]_0 = 3 \times 10^{-5}\ M$)

A. Dependence on Acid Concentration

$[HCl]_{total}$, *M*	$[HCl]_{undiss}$, M^a	$10^4 k_{obsd}$, sec^{-1}	$[HCl]_{total}$, *M*	$[HCl]_{undiss}$, M^a	$10^4 k_{obsd}$, sec^{-1}
0.453	0.317	3.97	1.70	1.41	15.3
0.850	0.653	8.40	1.98	1.67	17.9
1.14	0.909	10.6			

B. Dependence on Chloride Ion Concentration
($[HCl]_{total} = 0.524\ M$, $\mu = 1.0$)

$[Cl^-]$, *M*	$10^4 k_{obsd}$, sec^{-1}	$[Cl^-]$, *M*	$10^4 k_{obsd}$, sec^{-1}
0.0	3.07	0.408	5.65
0.202	4.26	0.603	6.72

[a] Calculated using $K_a = 0.059$.

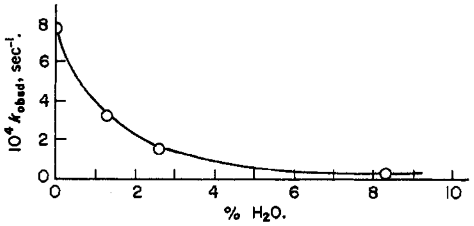
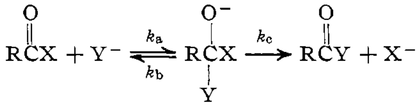


Figure 2.—Dependence of observed rate constant on water content for acid cleavage of $CH_3Mn(CO)_5$ in methanol.

A cleavage reaction occurs with the Lewis acid $HgCl_2$. The rate of reaction to form CH_3HgCl and $ClMn(CO)_5$ is first order in each reagent with a second-order rate constant of $1.1 \times 10^{-2}\ M^{-1}\ sec^{-1}$ at 25°. This is about a tenfold increase over the rate with HCl. $Hg(OAc)_2$ is even more reactive.

Discussion

Cleavage of $CH_3COMn(CO)_5$.—$CH_3COMn(CO)_5$ exhibits behavior which is similar to that of esters of strongly basic alcohols and amides. For the organic acyl derivatives, the mechanism of reaction with nucleophiles involves the two-step mechanism[25]



$$\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{X} + \mathrm{Y}^- \underset{k_b}{\overset{k_a}{\rightleftharpoons}} \mathrm{R}\underset{\underset{\mathrm{Y}}{|}}{\overset{\mathrm{O}^-}{\overset{|}{\mathrm{C}}}}\mathrm{X} \xrightarrow{k_c} \mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Y} + \mathrm{X}^- \qquad (7)$$

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TABLE III

SECOND-ORDER RATE CONSTANTS FOR THE ALKALINE HYDROLYSIS OF ACETYL DERIVATIVES

$$CH_3COX + OH^- \longrightarrow CH_3CO_2^- + HX$$

X	k_2, M^{-1} sec^{-1} (at 25°)	Rel rate	Ref
NH_2	3.7×10^{-3}	1	29
$Mn(CO)_5$	0.025	680	This work
OCH_3	0.152	4100	30
OC_6H_5	1.15	31,000	31a
$OC_6H_4NO_2$	14.8	400,000	31b

Using the steady-state approximation for the intermediate it can be shown that

$$-\frac{d[RCOX]}{dt} = \frac{k_a}{(k_b/k_c) + 1}[RCOX][Y^-] \qquad (8)$$

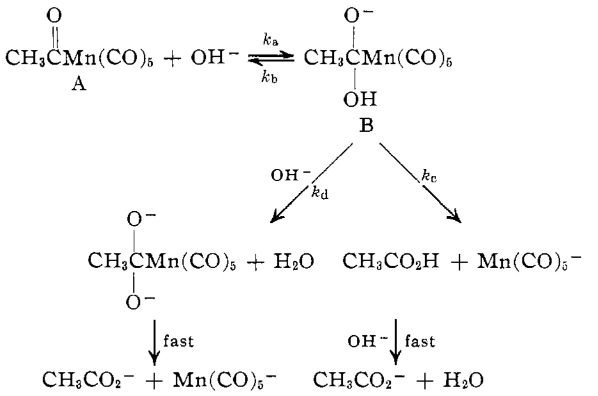
The reaction will exhibit second-order kinetics, but the observed rate constant depends on two parameters—the rate constant for formation of the intermediate (k_a) and the partitioning of the intermediate (k_b/k_c).

The reaction of $CH_3COMn(CO)_5$ with $NaOCH_3$ is first order in each reagent and apparently follows the same mechanism. Investigation of a variety of acylmetal compounds has shown the leaving-group effect of eq 5. The basicity of these anions increases in the opposite order[26]

$$Co(CO)_4^- \ll Mn(CO)_5^- \sim Co(CO)_3(P(C_6H_5)_3)^- \ll Fe(CO)(P(C_6H_5)_3)(C_5H_5)^- \qquad (9)$$

These results are consistent with the addition–elimination mechanism. The more basic anions will be more difficult to displace, so partitioning of the intermediate will favor a return to reactants (k_b/k_c is large). From eq 8, this will lead to a decrease of k_{obsd}. Trifluoroacetylmanganese pentacarbonyl reacts much faster with $NaOCH_3$ than does $CH_3COMn(CO)_5$. The effects of substituents in the acyl group will effect k_b and k_c to approximately the same extent, but electron-withdrawing groups will increase k_a, the rate of nucleophilic attack on the carbonyl carbon.

Since most data on organic acyl derivatives have been determined for aqueous systems, the alkaline hydrolysis of acetylmanganese pentacarbonyl was studied. Simultaneous second- and third-order paths were observed. A reasonable mechanism consistent with these data is shown in the equation



(10)

Using the steady-state approximation for B it can be shown that

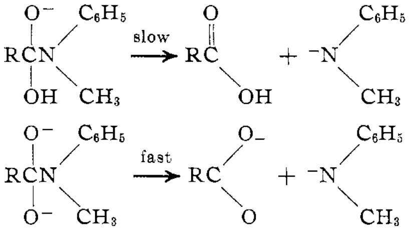
$$-\frac{d[A]}{dt} = \frac{k_a k_c[A][OH^-] + k_a k_d[A][OH^-]^2}{k_b + k_c + k_d\,[OH^-]} \qquad (11)$$

When A and B are in equilibrium, *i.e.*, $k_b \gg k_c + k_d[OH^-]$, the rate law simplifies to

$$-\frac{d[A]}{dt} = \{k_c[OH^-] + k_d[OH^-]^2\}\frac{k_a}{k_b}[A] \qquad (12)$$

The part of the reaction that is first order in $[OH^-]$ involves a mechanism totally analogous to the reaction with methoxide ion. However, the intermediate B has an acidic proton which is not present following attack by $^-OCH_3$. Removal of this proton by OH^- provides an extra driving force to cleave the carbon–metal bond.

A third-order path has often been found for the hydrolytic reactions in which the leaving group is difficult to displace. A number of examples of this type of behavior have been reported[27] in the hydrolytic cleavage of carbon–carbon bonds in activated ketones, $RCOCH_2X$. Among the carboxylic acid derivatives, this type of behavior has been observed for *N*-methylanilides.[28] The extra stabilization of the carboxylate ion compared to the carboxylic acid acts to lower the activation energy for the decomposition of the intermediate (see eq 13). The conclusion is that, like NR_2^-, the manganese pentacarbonyl anion is a poor leaving group and needs extra driving force to break the carbon–metal bond. A quantitative comparison of the ease of alkaline cleavage of $CH_3COMn(CO)_5$ relative to other acetyl derivatives is presented in Table III.[29–31] The second-order rate constant for base hydrolysis of $CH_3COMn(CO)_5$ is much faster than the rate of acetamide but slower than the rates for most esters.



(13a)

(13b)

Other Nucleophiles.—We have determined the reactivity of a variety of nucleophiles toward $CH_3COMn(CO)_5$. The subject of nucleophilic reactivity and nucleophilic catalysis in the reactions of organic acyl derivatives has been reviewed by Bender.[25] The studies of Jencks and Carriuolo[31] on *p*-nitrophenyl acetate have shown that the most reactive nucleophiles are hydroperoxide ion, hypochlorite ion, OH^-, ethylenediamine, hydroxylamine, and imidazole. Slower but measurable rates are observed with pyridine, HPO_4^{2-}, F^-, and $CH_3CO_2^-$.

We observed no cleavage of $CH_3COMn(CO)_5$ with imidazole, pyridine, $NH_2C_6H_{11}$, NH_3, HPO_4^{2-}, F^-, $CH_3CO_2^-$, or NO_3^-. $CH_3COMn(CO)_5$ is susceptible to

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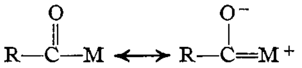
attack only by very strong proton bases such as OCH_3^- and OH^- and by hydroxylamine which is known to be abnormally reactive toward organic acyl compounds.[30] These results are in accord with Bender's selectivity–reactivity relationship.[25] More reactive derivatives are susceptible to attack by a wide range of nucleophiles, but the less reactive compounds react with only a limited number of nucleophiles. Again, $CH_3COMn(CO)_5$ behaves like an amide or an ester of a basic alcohol.

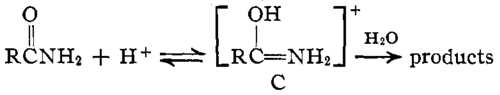
The lack of reactivity of $CH_3COMn(CO)_5$ with most nucleophiles can also be understood by consideration of the bonding of the carbon to the metal. There is significant π bonding between the metal and the acyl carbonyl group due to overlap of a filled d orbital of the metal with an empty π^* orbital of the carbonyl group. This can be pictured as



$$R{-}\overset{O}{\overset{\|}{C}}{-}M \longleftrightarrow R{-}\overset{O^-}{\overset{|}{C}}{=}M^+$$

Such an interaction has long been used to account for the low CO stretching frequencies found for these compounds.[32] The abnormally short acyl carbon–metal bond distance in $CH_3COMo(CO)_2(P(C_6H_5)_3)(C_5H_5)$ has been attributed to π bonding.[33] Since π bonding is lost upon formation of a four-coordinate carbon atom, the activation energy for nucleophilic attack is high.

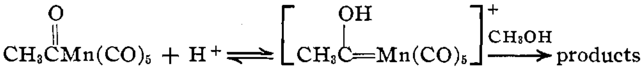
Acid-Catalyzed Solvolysis.—The acid-catalyzed solvolysis of $CH_3COMn(CO)_5$ also exhibits behavior similar to that of amides.[25] The rate of hydrolysis of acetamide is initially proportional to the hydrogen ion concentration but levels off and reaches a maximum rate at a sulfuric acid concentration of ~3 *M*. The rate then begins to decrease at higher acid concentrations. These results are readily explained by a mechanism involving protonation of the acyl oxygen atom



$$R\overset{O}{\overset{\|}{C}}NH_2 + H^+ \rightleftharpoons \underset{C}{\left[R\overset{OH}{\overset{|}{C}}{=}NH_2\right]^+} \xrightarrow{H_2O} \text{products} \quad (14)$$

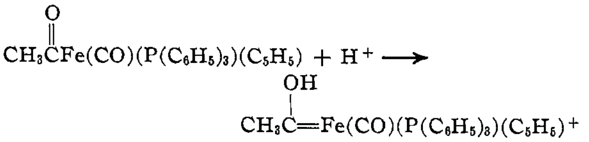
Below the maximum rate, increasing acid strength increases the concentration of the protonated intermediate C. Once the rate maximum has been achieved, all of the amide has been protonated, and further increases in the acid concentration serve only to decrease the concentration of activity of water.

The results with $CH_3COMn(CO)_5$ in methanol are similar and a similar mechanism is operative



$$CH_3\overset{O}{\overset{\|}{C}}Mn(CO)_5 + H^+ \rightleftharpoons \underset{D}{\left[CH_3\overset{OH}{\overset{|}{C}}{=}Mn(CO)_5\right]^+} \xrightarrow{CH_3OH} \text{products} \quad (15)$$

One difference between these two systems must be emphasized. With acetamide in water the rate increases linearly as $[H^+]$ is changed over several orders of magnitude and the rate maximum is achieved only in very strong acid solutions (~3 *M*). With $CH_3COMn(CO)_5$ in methanol, curvature is apparent from the outset and the rates start leveling off even at an acid concentration of 0.1 *M*. This implies that the preequilibrium for the formation of the protonated intermediate is much more favorable for $CH_3COMn(CO)_5$ than for CH_3CONH_2. This result is not too surprising in view of the π bonding discussed above. The intermediate D is a metal–carbene complex; due to participation of d electrons in π bonding, this intermediate would be expected to be quite stable. In fact, Green and Hurley[34] have prepared a stable carbene by protonation of $CH_3COFe(CO)(P(C_6H_5)_3)(C_5H_5)$ in hydrocarbon solvent



$$CH_3\overset{O}{\overset{\|}{C}}Fe(CO)(P(C_6H_5)_3)(C_5H_5) + H^+ \longrightarrow CH_3\overset{OH}{\overset{|}{C}}{=}Fe(CO)(P(C_6H_5)_3)(C_5H_5)^+ \quad (16)$$

Cleavage of $CH_3Mn(CO)_5$.—The rate of acid cleavage of $CH_3Mn(CO)_5$ depends on the concentration of the acid but is significantly increased by addition of chloride salts. Chloride ion itself does not react with $CH_3Mn(CO)_5$ in methanol. Water caused a remarkable decrease in the rate of cleavage. Water causes the dissociation of HCl and also reduces the activity of the acid by strong solvation.

Other acids were not as effective as HCl. $HClO_4$ is totally dissociated in methanol and exhibited no activity. Acetic acid is undissociated but is a poor proton donor; it was also unreactive. All these results show behavior which is analogous to that observed for acid cleavage of organomercurials.[11]

Possible detailed mechanisms have been given many times previously.[8,11,35] In the present case of a transition metal of low oxidation state, an oxidative addition mechanism, similar to that of Belluco[13] for platinum(II) complexes, seems most attractive. That is, addition of HCl to a filled d orbital of the metal is followed by reductive elimination of HCH_3. The intermediate, a manganese(III) complex which is eight-coordinated, would have only transient existence.

The same kind of mechanism could apply to the cleavage reactions of $HgCl_2$ and $Hg(OAc)_2$. The fact that the mercury salts are better cleaving agents than HCl is consistent with bonding of mercury either to carbon or to manganese in the rate-determining step. Cleavage of alkyl groups from transition metals by halogens could also involve an oxidative addition mechanism. It should be noted that this mechanism predicts[36] the retention of configuration at carbon commonly observed in such electrophilic substitution reactions.[8,24]

Johnson and Winterton have reported that the acid hydrolysis of 4-pyridiomethylmanganese pentacarbonyl goes by a dissociation mechanism, independent of hydrogen ion and chloride ion concentration[37]

$$^+HNC_5H_4CH_2Mn(CO)_5 \longrightarrow {}^+HNC_5H_4CH_2^- + Mn(CO)_5^+ \quad (17)$$

The difference in behavior may be attributed to the slow rate of the acid-catalyzed reaction in water (Figure 2) and to the large resonance stabilization of the protonated pyridiomethyl carbanion. It is not surprising that the related 3-pyridiomethylmanganese complex decomposes by a free-radical mechanism, since resonance stabilization is greatly reduced.[37]

Acknowledgment.—This work was supported by a grant from the U. S. Atomic Energy Commission and by an NIH predoctoral fellowship to R. W. J.

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