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NEW OBSERVATIONS ON CARBON MONOXIDE INSERTION REACTIONS

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Particular interest has been recently shown for carbon monoxide insertion reactions. The interest in this field was originated by the important observation[1] that alkylmanganesepentacarbonyls can be transformed into the corresponding acylmanganesepentacarbonyl derivatives

$$RMn(CO)_5 + CO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RCOMn(CO)_5 \tag{1}$$

under CO pressure. Later it was found[2] that reaction (1) can occur even at ordinary pressure using solvents of reasonably high dielectric constant and this opened the way to obtain reliable kinetic and thermodynamic data for the reaction.

Coffield and coworkers[3] showed that by carrying out reaction (1) with labelled ^{14}CO an acylmanganesepentacarbonyl with an unlabelled ketonic group was obtained. This experiment clearly indicated that the CO to be inserted in between the carbon–metal bond did not come directly from the gas phase. Indirect confirmation for this as yet unpublished isotopic experiment came from the discovery that the formation of acylmanganesecarbonyls from alkylmanganesepentacarbonyls could take place using nucleophiles (L) other than carbon monoxide, such as amines[4,5] and triphenylphosphine[5,6]:

$$RMn(CO)_5 + L \rightleftharpoons RCOMn(CO)_4L \tag{2}$$

Recently it has been found[7] that reaction (2) is of a completely general character and, for example, can also be carried out with charged nucleophiles, such as I^-:

$$CH_3Mn(CO)_5 + LiI \rightleftharpoons [CH_3COMnI(CO)_4]Li \tag{3}$$

The lithium salt obtained by reaction (3) has actually been isolated in a pure state. Infrared evidence also exists that reactions similar to (3) take place with other charged nucleophiles such as OCH_3^-, SCN^- and CN^-.

With this new information, the possibility of studying the influence of the nucleophile on reactions of type (2) has been considerably increased. The kinetic data available until now included reactants (CO, PPh_3, amines) whose nucleophilic power is probably not very different. Reaction (1), with $R = CH_3$, was found[2] to be first order both in $CH_3Mn(CO)_5$ and CO in 2,2′-diethoxydiethylether. The same order was also found[5] for the reaction of $CH_3Mn(CO)_5$ with cyclohexylamine in non-polar solvents. An apparent change in the reaction mechanism was however observed in the case of the reaction of $CH_3Mn(CO)_5$ with amines[5] and triphenylphosphine[6] in 2,2′-diethoxydiethylether. Both these reactions were found to be independent of the ligand concentration, the explanation proposed[6] being that a solvent-assisted mechanism was operating in these cases. To answer the question whether carbonylation reactions give most commonly second-order or first-order kinetics which is very relevant for an understanding of the reaction mechanism, it appeared desirable to expand the range of nucleophiles under investigation.

Reaction (3) is very fast, and therefore rather difficult to study by classical methods. To avoid some of the experimental difficulties, the reaction of $CFH_2Mn(CO)_5$ with lithium iodide was studied. The fluoro-compound was found to give a much slower carbonylation reaction, in agreement with the previously determined[8] substituent-effect on the rates of reaction (1). The kinetics of the reaction of $CFH_2Mn(CO)_5$ with lithium iodide were studied spectroscopically in pseudo-first order conditions (with a large excess of the nucleophile). The results are contained in Fig. 1, where first-order plots of concentrations *vs.* time are shown for three different concentrations of lithium iodide with ionic strength kept constant by addition of $LiPF_6$. This result shows that the reaction of $CFH_2Mn(CO)_5$ with LiI is substantially a second-order process. However, a pseudo-first order, solvent-assisted, mechanism is probably operating simultaneously. This is sup-

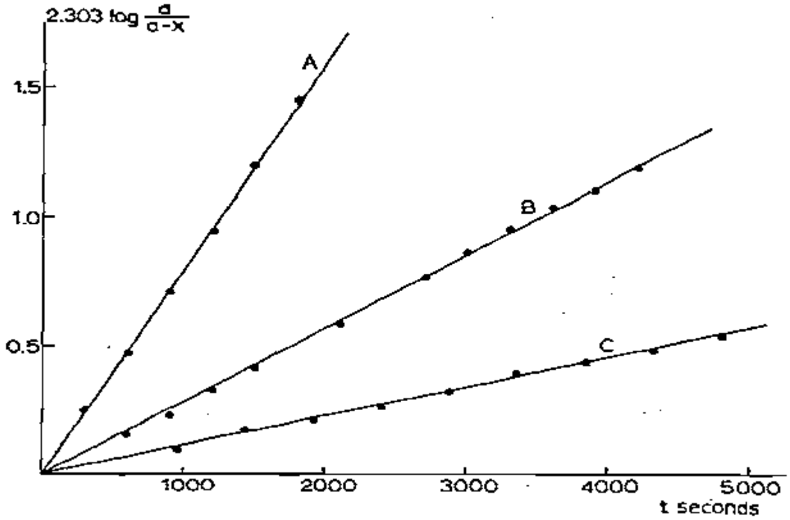


Fig. 1. Plots showing the iodide dependence of the reaction $CFH_2Mn(CO)_5 + LiI \rightleftharpoons [CFH_2CO\text{-}MnI(CO)_4]Li$ in 2,2′-diethoxydiethylether at 30°. $[CFH_2Mn(CO)_5]_0$, 0.01 *M*. Initial concentrations of LiI are: A) 0.48 *M*; B) 0.24 *M*; C) 0.12 *M*. The ionic strength was kept constant at 0.48 by addition of $LiPF_6 \cdot THF$.

ported by the fact that in kinetic runs carried out at about $3 \cdot 10^{-3}$ M concentration of both $CH_3Mn(CO)_5$ and LiI or with two or three-fold excess of lithium iodide, the disappearance of methylmanganesepentacarbonyl was found to follow quite closely a first-order kinetic equation. Similar kinetic experiments carried out at about 10^{-2} M concentration of $CH_3Mn(CO)_5$ fit a second-order kinetic equation better with a rate constant $4 \cdot 10^{-1}$ sec^{-1} l. mole^{-1} at 25°; *i.e.* about hundred times bigger than the rate constant[2] k_1 of reaction (1) at 20° ($3.89 \cdot 10^{-3}$ sec^{-1} l. mole^{-1}).

From the present and previous studies, it appears therefore that the reactions of alkylmanganesepentacarbonyls with different nucleophiles usually follow second-order kinetics. Pseudo first-order reactions can however occur in the case of solvation of the intermediate. Second-order kinetics are consistent both with a mechanism of the type

$$RMn(CO)_5 \overset{\text{rapid}}{\rightleftharpoons} RCOMn(CO)_4 \xrightarrow{+\text{L (slow)}} RCOMn(CO)_4L \tag{4}$$

or with the direct displacement reaction of the S_N2 type

$$RMn(CO)_5 + L \xrightarrow{\text{slow}} RCOMn(CO)_4L \tag{5}$$

whereas a dissociative mechanism of the S_N1 type

$$RMn(CO)_5 \xrightarrow{\text{slow}} RCOMn(CO)_4 \xrightarrow{+\text{L (fast)}} RCOMn(CO)_4L \tag{6}$$

appears not to be the prevailing one. Mechanism (5) or a similar one in which L is a solvent molecule, is the preferred one.

In view of this, it appeared interesting to investigate also the reaction of acetylmanganesepentacarbonyl with different nucleophiles:

$$CH_3COMn(CO)_5 + L \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} CO + CH_3COMn(CO)_4L \tag{7}$$

The products of the reaction are the same as those from reaction (2) the only difference being that CO is evolved. The latter can be measured and therefore the kinetics studied gas-volumetrically.

Reactions (7) do not usually go to completion. This fact, and also some further complications make their study difficult and the interpretation of their kinetic data rather elaborate. The acetyl-derivative $CH_3COMn(CO)_4P(C_6H_5)_3$ decarbonylates partially to the corresponding methyl compound $CH_3Mn(CO)_4$-$P(C_6H_5)_3$ even at room temperature; in the case of the amines at RNH_2/CH_3-$COMn(CO)_5$ ratios higher than one, back absorption of carbon monoxide has been observed over long reaction times, suggesting the occurrence of carbon monoxide addition to the amine with formation of alkylformamides. At high pressure and temperature, manganese has been found to catalyse the addition of CO to primary amines with formation of 1,3-dialkylureas; alkylformamides are probably the intermediates of this reaction[9].

The reaction with iodide ions is the simplest: no secondary products were observed and the equilibrium is shifted almost completely to the right under the conditions indicated in Table I.

TABLE I

REACTIONS OF ACETYLMANGANESEPENTACARBONYL WITH SOME NUCLEOPHILES

$CH_3COMn(CO)_5 + L \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} CO + CH_3COMn(CO)_4L$

in 2,2'-diethoxydiethylether at 30.5 °C; $[CH_3COMn(CO)_5]_0 = 0.06$ mole/l.

Reagent mole/l	*Rate constant*[a] *$10^5 \times k_7$ (sec^{-1})*	*Reference*
—	3.1[b]	2
$P(C_6H_5)_3$; 0.042	3.4	6
$C_6H_{11}NH_2$; 0.061	3.4[c]	this work
$C_4H_9NH_2$; 0.064	3.2[c]	this work
I^-; 0.061	3.2	this work

[a] Similar results were obtained over a wide range of nucleophile concentration.

[b] This is the rate constant k_{-1} for the reverse of reaction (1).

[c] This is for the rate of approach to equilibrium.

It appears clearly from the data of Table I that in each case reactions (7) are independent of nucleophile concentration and more important, they take place with the same rate constant (k_{-1}) previously found for the decarbonylation of $CH_3COMn(CO)_5$ (reverse of reaction (1)). This rate constant was found to be $3.1 \cdot 10^{-5}$ sec^{-1} at 30.5° in 2,2'-diethoxydiethylether. This suggests that the reverse of reaction (1) and reaction (7) take place by the same mechanism. However, there are two possible mechanisms to explain these experimental data.

$$\text{A)} \qquad CH_3COMn(CO)_5 \overset{\text{slow}}{\rightleftharpoons} CH_3COMn(CO)_4 + CO$$

$$CH_3COMn(CO)_4 + L \overset{\text{fast}}{\rightleftharpoons} CH_3COMn(CO)_4L$$

$$\text{B)} \qquad CH_3COMn(CO)_5 \underset{k_{-B}}{\overset{k'_B}{\rightleftharpoons}} CH_3Mn(CO)_5 + CO$$

$$CH_3Mn(CO)_5 + L \underset{k'_{-B}}{\overset{k'_B}{\rightleftharpoons}} CH_3COMn(CO)_4L$$

Mechanism A represents a typical dissociative mechanism of the S_N1 type in which a coordinately unsaturated manganesetetracarbonyl species is formed. In B a pre-equilibrium to $CH_3Mn(CO)_5$ is suggested, this being therefore the rate-determining step. By applying the steady state approximation to scheme B one gets the following expression for the rate of disappearance of $CH_3COMn(CO)_5$:

$$\frac{d[CH_3COMn(CO)_5]}{dt} = \\ = \frac{k_B[CH_3COMn(CO)_5] - \dfrac{k_{-B}k'_{-B}[CO]\,[CH_3COMn(CO)_4L]}{k'_B[L]}}{\dfrac{k_{-B}[CO]}{k'_B[L]} + 1}$$

It is readily seen that the disappearance of $CH_3COMn(CO)_5$ depends on [CH_3-$COMn(CO)_5$] only if: a) the CO concentration in the liquid phase is small and b) k'_B is large with respect to k_{-B} and k'_{-B}. Requirement a) is fulfilled in each case because we are operating at atmospheric pressure of carbon monoxide and the solubility of this gas in 2,2'-diethoxydiethylether is small; requirement b) is certainly met in the case of the reaction with lithium iodide, as discussed above. Furthermore, it must be mentioned that the reaction of $CH_3Mn(CO)_5$ with cyclohexylamine was found[5] to be independent of amine concentration in 2,2'-diethoxydiethylether, which certainly would help in obtaining first-order kinetics by a scheme of type B. Therefore, scheme B is also consistent with the kinetic data.

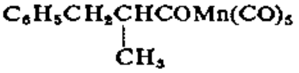
Scheme B does not necessarily mean, however, that $CH_3Mn(CO)_5$ as such is formed in the rate-determining step: it can simply mean that the ligand L does not attack acetylmanganesepentacarbonyl until the methyl group has migrated (see below the discussion concerning the *methyl migration* mechanism). Mechanism B is therefore considerably different from A since it also includes the possibility that the methyl group in the final product $CH_3COMn(CO)_4L$ is bonded to a ketonic group different from that to which it was attached in the original CH_3CO-$Mn(CO)_5$. It is, on the other hand, a necessary condition of scheme A that the methyl group remains bonded to the same ketonic carbonyl and no breaking of the metal–carbon bond occurs at any moment throughout the process.

An experiment carried out with an optically active acylmanganesepentacarbonyl should therefore give a reaction product $RCOMn(CO)_4L$ with retention of configuration if the reaction mechanism is A. By the pathway B either retention of configuration or racemization could occur.

Mechanism A: retention of configuration.

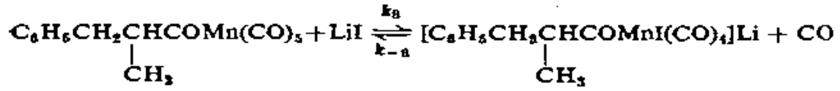
Mechanism B: retention or racemization.

The optically active manganese compound (+)-benzylmethylacetylmanganesepentacarbonyl



$$C_6H_5CH_2\underset{\substack{|\\CH_3}}{C}HCOMn(CO)_5$$

was prepared from the corresponding optically active acyl chloride and sodium pentacarbonylmanganate. It was reacted with lithium iodide in the conditions indicated in Table II. No change in the direction of rotation was observed.



$$C_6H_5CH_2\underset{\substack{|\\CH_3}}{C}HCOMn(CO)_5 + LiI \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} [C_6H_5CH_2\underset{\substack{|\\CH_3}}{C}HCOMnI(CO)_4]Li + CO \qquad (8)$$

Reaction (8) was also found to be independent of the lithium iodide concentration with a rate constant $k_8 = 8.5 \cdot 10^{-5}\ sec^{-1}$.

TABLE II

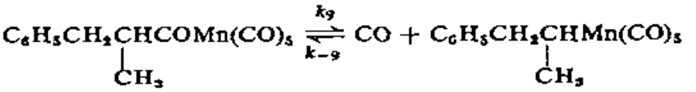
EXPERIMENTS WITH AN OPTICALLY ACTIVE ACYLMANGANESEPENTACARBONYL COMPOUND: (+)-BENZYL-METHYL-ACETYL-MANGANESEPENTACARBONYL

Temperature: 30°; Solvent: 2,2'-diethoxydiethylether.

Complex mole/l	*Lithium iodide mole/l*	*Reaction Time (h)*	*Initial** $[\alpha]_D^{30}$	*Final** $[\alpha]_D^{30}$
0.06	0.3	24	75.1[a]	153[b]
0.09	0.3	24	76.8[c]	146[d]
0.06	0.3	27	76.8[c]	140[e]
0.06	—	76	75.1[a]	74.9[f]
0.06	—	99	76.8[c]	74.8[f]

* The specific rotations were measured in 2,2'-diethoxydiethylether at the following concentrations (g/100 ml of solution):
a) 1.027; b) 1.04; c) 2.15; d) 1.27; e) 0.82; f) 2.08.

Since a decision between mechanism A or B was still not possible in view of this result, it was decided to investigate whether or not the conversion of the above mentioned optically active acylmanganesepentacarbonyl into the corresponding alkyl-derivative was stereospecific. This is in fact the *conditio sine qua non* for mechanism B to be considered as a real possibility. As shown from the data of Table II, the optically active acyl-compound is converted into the corresponding alkyl derivative with no change in the direction of rotation.



$$C_6H_5CH_2\underset{CH_3}{\underset{|}{C}}HCOMn(CO)_5 \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} CO + C_6H_5CH_2\underset{CH_3}{\underset{|}{C}}HMn(CO)_5$$

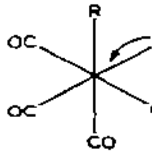
In order to avoid decomposition, the temperature of the experiment was kept rather low (30.0 °C), implying that the equilibrium was maintained on the acyl side (only about 10% of the CO expected for the total conversion was evolved). However, in view of the results of Table I, the rate constant of reaction (9) can be considered to be identical with k_8 of reaction (8) and the half-time of reaction (9) can be therefore calculated to be about 130 minutes. The conditions of *dynamic* equilibrium for reaction (9) were maintained for a very long time (three–four days) under a constant CO pressure of one atmosphere: despite the low conversion, the experiment is therefore significant and shows that both the forward and the back reactions (9) are stereospecific.

This experiment does not clarify our ideas about the mechanism of the reactions of $CH_3COMn(CO)_5$ with nucleophiles, but it has added something new and very valuble to our knowledge of carbonylation reactions. A plausible mechanism for the carbonylation reaction has to take into consideration the result of this experiment. If one assumes that the unchanged direction of rotation corresponds to retention of configuration, the experiments tell us that in the course of the alkyl migration the new carbon–carbon bond and the original carbon–manganese bond are formed and broken, respectively, on the same side of the alkyl group.

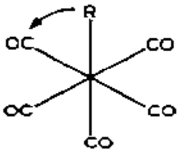
How the acetyl group is formed in the course of the carbonylation reaction (1) is another question.

Several mechanisms are possible, all reducible to two main types, namely the CO-insertion mechanism (*1*) and the methyl-migration mechanism (*2*). This latter was the one proposed earlier[8] for which Mawby, Basolo and Pearson have recently found[10] some additional evidence based mainly on stereochemical considerations of the final products obtained by a modified reaction of the type (2).

Although mechanism (*2*) of methyl-migration appears to be the most likely, some details are still to be investigated.



(*1*)

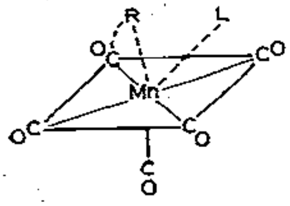


(*2*)

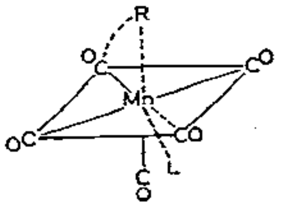
An important question is the following: in which position, with respect to the alkyl group, does the ligand attack the central metal atom to give the acylated product? To clarify this point, a reaction of type (2) in which L is a ligand different from CO will be studied. We have, in fact, found[7] recently that both *cis* and *trans* geometrical isomers are obtained by a reaction of this type carried out with iodide ions or triphenylphosphine. This was indicated by the infrared spectra of the reaction products in the terminal CO region and especially by the presence of two acetyl proton resonances between 7 and 8 τ.

It would be necessary, in order to answer the question concerning the position of attack by the ligand, to identify the infrared bands or the n.m.r. peaks due to the geometrical isomers, then follow the course of reaction (2) and see which of the two geometrical isomers is formed *first*. The examination of the initial products of reaction, rather than the study of the final products is necessary in this case because successive isomeric rearrangements in solution are possible. Of the several ways of attack by the ligand which can be envisaged to operate in the methyl-migration mechanism, two appear the most likely, as shown below.

In mechanism (*3*) the attack by the nucleophile takes place on the same side of the alkyl group: a *cis*-product is expected to result by such an attack. If *trans*-



(*3*)



(*4*)

effect has some importance in octahedral complexes, a mechanism of type *(4)* in which the nucleophile attacks the metal from below the equatorial plane should also be taken into consideration: the *trans*-isomer can then possibly, but not necessarily, be the product of reaction.

ADDED IN PROOF

Kraihanzel and Maples[11] have recently reported that, on the basis of infrared and n.m.r. data, the first product observed in the reaction of $CH_3Mn(CO)_5$ with $P(C_6H_5)_3$ appears to be *trans*-$CH_3COMn(CO)_4P(C_6H_5)_3$.

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