A Kinetic Study of the Reactions of Methyl- and Acetyl-pentacarbonylmanganese with Acetylenes

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The reaction between [MnMe(CO)$_5$] and dimethyl acetylenedicarboxylate to give $[\overline{\text{Mn}\{Z\text{-MeO}_2\text{CC=C(CO}}\text{Me)-CO}_2\text{Me}\}(\text{CO})_4]$ has been studied under pseudo-first-order conditions in various solvents and has been found to obey the rate law, rate = $k_1 + k_2[\text{MeO}_2\text{CC}_2\text{CO}_2\text{Me}]$. The k_1 term arises from a ' solvent-assisted ' two-step methyl to acetyl migratory-insertion reaction, while the k_2 term arises from a direct second-order reaction in which the electron-deficient acetylene appears to stabilize the transition state for methyl to acetyl migration. The reaction between [Mn(COMe)(CO)$_5$] and MeO$_2$CC$_2$CO$_2$Me is first-order in the manganese complex, but independent of acetylene concentration consistent with a rate-determining step involving CO ligand dissociation.

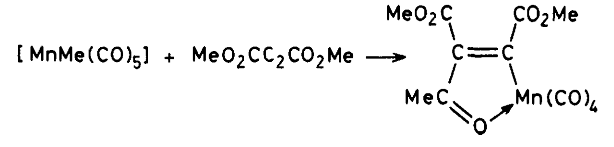
THERE have been several kinetic studies on the reactions of alkylpentacarbonylmanganese complexes in which alkyl to acyl migration occurs on reaction with a ligand L.[1,2] In every case studied to date these reactions can be explained by a two-step mechanism in which the first step is the reversible alkyl migration to form a co-ordinatively unsaturated acyl complex, equation (i).

$$[\text{MnR(CO)}_5] \underset{k_{-\text{A}}}{\overset{k_\text{A}}{\rightleftharpoons}} [\text{Mn(COR)(CO)}_4] \xrightarrow{k_\text{B}\,(+\text{L})} [\text{Mn(COR)(CO)}_4\text{L}] \qquad \text{(i)}$$

Applying steady-state conditions this leads to the general expression (ii) for the overall rate constant of the reaction, and the rate law observed for any particular reaction depends upon the nature of L, and whether or not the solvent plays any part in the reaction.

$$k_\text{obs.} = \frac{k_\text{A}k_\text{B}[\text{L}]}{k_{-\text{A}} + k_\text{B}[\text{L}]} \qquad \text{(ii)}$$

In all the reactions so far investigated the ligand L has been a nucleophilic ligand, such as CO,[3] phosphines,[4] phosphites,[4,5] amines,[4] and I$^-$.[6]



(1)

Several years ago we described the reaction of pentacarbonylmethylmanganese with dimethyl acetylenedicarboxylate (dmad) which affords the stable (vinyl ketone)manganese complex (1).[7] We postulated at the time that these reactions probably involved as the rate-determining step the methyl to acetyl migration either under the influence of the acetylene ligand or by a solvent-assisted migration. With this reaction there was the opportunity to study for the first time an alkyl migration reaction in which the attacking ligand L is an electrophile rather than a nucleophile. We now report the results of a kinetic study of this reaction.

TABLE 1

Kinetic results for the reaction of [MnMe(CO)$_5$] with dmad in diethyl ether at 25.0 ± 0.1 °C

10^3[MnMe(CO)$_5$]/ mol dm^{-3}	10^3[dmad]/ mol dm^{-3}	$10^4k_\text{obs.}$/s^{-1}
0.02	0.20	0.22
0.02	0.50	0.31
0.02	1.00	0.44
0.02	1.62	0.63
0.03	0.50	0.32
0.03	0.75	0.40
0.03	1.50	0.59

RESULTS AND DISCUSSION

The kinetics of the reaction between [MnMe(CO)$_5$] and dmad were followed by studying the rate of disappearance of the highest frequency (A_1) band at 1 991 cm^{-1} in the metal–carbonyl region of the i.r. spectrum in various solvents at 25.0 ± 0.1 °C. In all the reactions studied, pseudo-first-order conditions were used with a ten-fold molar excess of dmad. There was acceptable agreement between the rate of disappearance of [MnMe(CO)$_5$] and the rate of appearance of a band at 1 968 cm^{-1} due to the formation of (1). There was a quantitative agreement between the final absorbances of peaks in the metal–carbonyl region due to (1) and the absorbances calculated for (1) based on the absorption coefficients of these bands and the concentration of the starting material. This indicates that reaction proceeds to completion, and there was no evidence for any side reactions. Over the rather limited range of initial concentrations of [MnMe(CO)$_5$] studied, the reactions all conformed to first-order kinetics for up to 75% complete reaction and the observed rate constants for the reaction in diethyl ether are given in Table 1; these rate constants were found to be reproducible to within ±5%, and the standard deviations of these results were within ±2.5%. A plot of $k_\text{obs.}$ *versus* [dmad] gave a good straight line (Figure 1) showing that the reaction was not only first-order in [MnMe(CO)$_5$], but was also dependent upon [dmad] according to the rate law (iii).

$$k_\text{obs.} = k_1 + k_2[\text{dmad}] \qquad \text{(iii)}$$

Values of k_1 and k_2 were computed from the slope and intercept respectively and are given in Table 2.

The results can be accommodated by a mechanism in which the rate-determining formation of an intermediate (2) (see Scheme 1) occurs by competing dissociative (k_1)

TABLE 2

Rate parameters for the reaction of $[MnMe(CO)_5]$ with dmad in diethyl ether at 25.0 ± 0.1 °C

$10^3[MnMe(CO)_5]$/mol dm^{-3}	$10^4k_1/s^{-1}$ *	$10^4k_2/dm^3$ mol^{-1} s^{-1}
0.2	0.16 ± 0.01	0.29 ± 0.01
0.3	0.18 ± 0.03	0.27 ± 0.03

* From least-squares analysis of the results in Table 1.

TABLE 3

Rate parameters for the reaction of $[MnMe(CO)_5]$ with dmad in diethyl ether at different temperatures *

θ_c/°C	$10^4k_1/s^{-1}$	$10^4k_2/dm^3$ mol^{-1} s^{-1}
21.5	0.10 ± 0.03	0.25 ± 0.04
25.0	0.16 ± 0.01	0.29 ± 0.01
28.0	0.21 ± 0.03	0.47 ± 0.04
32.0	0.26 ± 0.05	0.67 ± 0.08

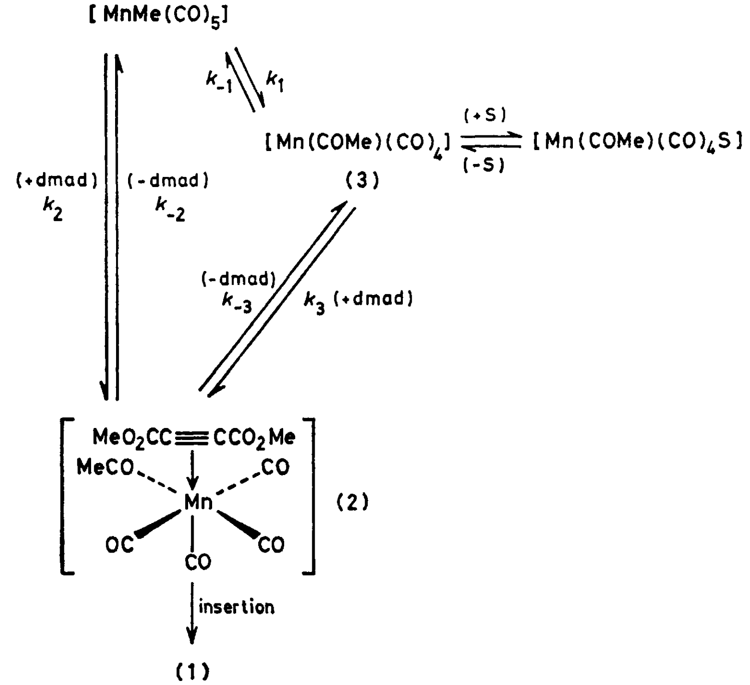
* $[MnMe(CO)_5] = 0.02 \times 10^{-3}$ mol dm^{-3}.

and associative (k_2) pathways. Assuming a steady-state concentration for the intermediate (3) this would lead to

$$\frac{-d[MnMe(CO)_5]}{dt} = \frac{k_1k_3[MnMe(CO)_5][dmad]}{k_{-1} + k_3[dmad]} + k_2[MnMe(CO)_5][dmad] \quad \text{(iv)}$$

the rate expression (iv) assuming that the collapse of (2) to the product (1) by a *cis* insertion of the η^2-acetylene ligand into the Mn-C(acetyl) bond is fast and irreversible, and also assuming that k_{-2} is negligible. If it is also assumed that k_{-1} is small such a mechanism would lead to the observed rate law[1] (v) where $k_{obs.} = k_1 + k_2[dmad]$.

$$\frac{-d[MnMe(CO)_5]}{dt} = k_{obs.}[MnMe(CO)_5] \quad \text{(v)}$$



SCHEME 1 S = solvent

From variable-temperature studies (Table 3) the activation parameters for the k_1 path have been calculated to be $\Delta H_1^{\ddagger} = 15 \pm 3$ kcal mol^{-1}, $\Delta S_1^{\ddagger} = -28 \pm 8$ cal K^{-1} mol^{-1}, and for the k_2 path $\Delta H_2^{\ddagger} = 18 \pm 3$ kcal mol^{-1}, $\Delta S^{\ddagger} = -17 \pm 8$ cal K^{-1} mol^{-1}.* These parameters were measured over a temperature range of only 10.5 °C and should be treated with some reservations, but they are of the same order of magnitude as those found previously for insertion reactions of $[MnMe(CO)_5]$.[4]

The relative importance of the k_1 and k_2 pathways depends upon the solvent used for the reaction (Table 4). In the non-polar solvent, benzene, the k_1 path is suppressed, and the reaction occurs mainly *via* the direct second-order pathway. On changing to diethyl ether and dichloromethane the k_1 path competes more effectively with the k_2 path, although dichloromethane appears to enhance the rate of the k_2 path, also. With the solvents tetrahydrofuran and nitromethane plots of $k_{obs.}$ *versus* [dmad] (Figure 2) were no longer linear, and the dependence of the rate on [dmad] tended towards a limiting value. This suggests that in these solvents the solvent competes with dmad for the intermediate (2) and k_3[dmad] becomes comparable to k_{-1}; the k_2 pathway is effectively suppressed in these solvents. Under these conditions $k_{obs.}$ is given by the expression (vi)[1,2]

$$k_{obs.} = \frac{k_1k_3[dmad]}{k_{-1} + k_3[dmad]} \quad \text{(vi)}$$

and increases with [dmad], approaching a limiting value at high concentrations. Support for this assumption

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* Throughout this paper: 1 cal = 4.184 J.

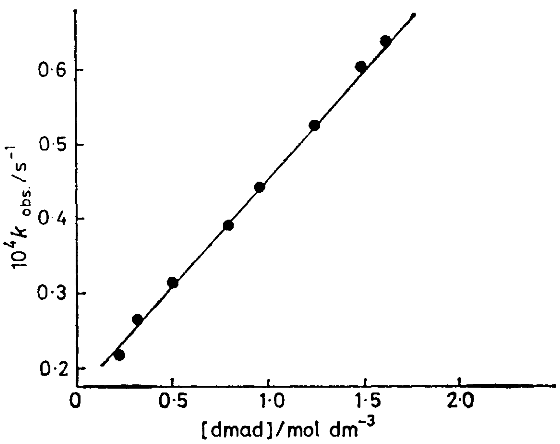


FIGURE 1 Dependence of $k_{obs.}$ on [dmad] for the reaction of [MnMe(CO)$_5$] (0.02 × 10^{-3} mol dm^{-3}) with dmad in diethyl ether at 25 °C

comes from the plots $1/k_{obs.}$ *versus* 1/[dmad] (Figure 3) which give good straight lines. That the rate of the k_1 path is enhanced over that of the k_2 path in nitromethane has been demonstrated by the addition of increasing amounts of nitromethane to the reaction mixture of [MnMe(CO)$_5$] and dmad in diethyl ether at 25.0 °C.

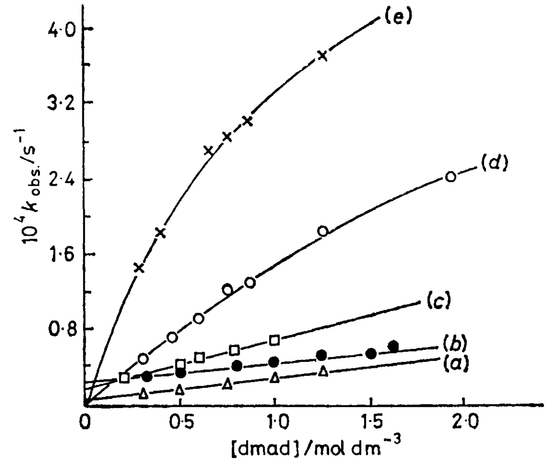


FIGURE 2 Dependence of $k_{obs.}$ on [dmad] for the reaction of [MnMe(CO)$_5$] with dmad in (*a*) benzene, (*b*) diethyl ether, (*c*) dichloromethane, (*d*) tetrahydrofuran, and (*e*) nitromethane at 25 °C

From the plot of $k_{obs.}$ *versus* [CH_3NO_2] (Figure 4) it can be seen that there is a reasonable linear relationship with the concentration of nitromethane. 'Solvent-assisted' methyl to acetyl migrations are well known,[1,2] but the reasons for this effect are not completely understood. It is usually assumed that in solvents of high donicity the solvent can compete with the ligand, in this case dmad, for the co-ordinatively unsaturated intermediate (3) as shown in Scheme 1. However, there seems no very obvious reason why this should lead to an overall increase in the rate of reaction unless the acetylene ligand can easily displace the solvent molecule directly to give (2) without intermediate formation of (3). It might be anticipated that if the solvent is a good donor ligand and is tightly bound to the metal the overall rate of product formation should decrease rather than increase.

Evidence that the k_2 pathway involves direct attack of an acetylene molecule on [MnMe(CO)$_5$] rests not only upon the observed rate law for the reaction with dmad, but also upon the effect that changing the acetylene derivative has upon the rate of this reaction. The kinetics of a number of reactions of [MnMe(CO)$_5$] with different acetylenes have been studied in diethyl ether as solvent at 25.0 °C. In the majority of cases the reactions were followed by measuring the rate of disappearance of [MnMe(CO)$_5$], but in a few cases where the resolution of the band at 1 991 cm^{-1} was poor the rate of formation of the product was monitored. No attempt was made to isolate the products from these reactions, but in every case the changes in the i.r. spectra observed throughout the kinetic runs were consistent with the formation of a product of type (1). Also, the products from the reactions of $HO_2CC_2CO_2H$ [7] and $HOCH_2C_2CH_2OH$ [8] have been isolated previously in high yields from reactions

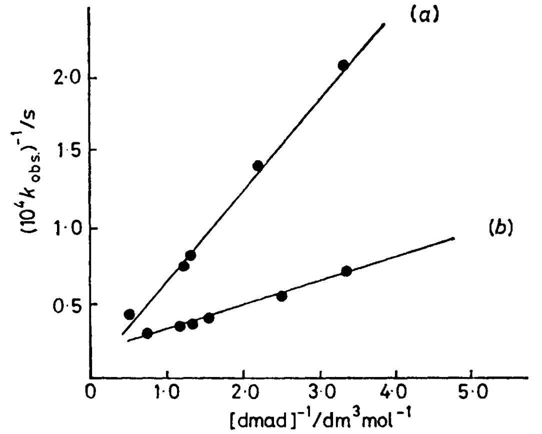


FIGURE 3 Plot of $k_{obs.}^{-1}$ *versus* [dmad]$^{-1}$ in (*a*) tetrahydrofuran and (*b*) nitromethane for the reaction of [MnMe(CO)$_5$] with dmad at 25 °C

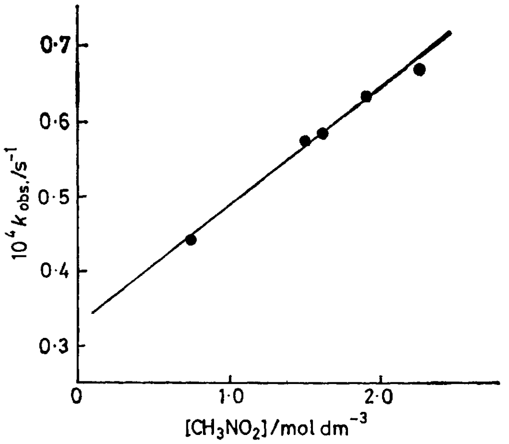


FIGURE 4 Dependence of $k_{obs.}$ on [CH_3NO_2] for the reaction of [MnMe(CO)$_5$] with dmad in diethyl ether–nitromethane at 25 °C

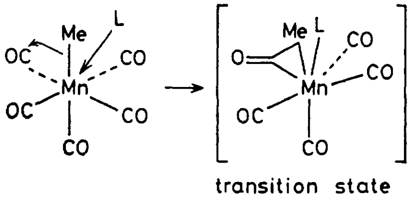
carried out under similar conditions, and they have been fully characterised. All the reactions were carried out under pseudo-first-order conditions and were found to follow the same rate law as that found with dmad. The values of k_1 and k_2 obtained from the plots of $k_{obs.}$ *versus* [acetylene] are given in Table 5. From these results it can be seen that while the k_1 pathway shows no obvious dependence on the nature of the acetylene, the rate of the associative reaction decreases in the order $HO_2CC_2CO_2H > EtO_2CC_2CO_2Et > HOCH_2C_2CH_2OH > ClCH_2C_2CH_2Cl \gg CH_3C_2CH_3 > PhC_2Ph$. The reactions of but-2-yne and PhC_2Ph are so slow that reaction was not complete even after 20 days. This trend is exactly that predicted on the basis of a molecular orbital study of the methyl migration reactions of $[MnMe(CO)_5]$ carried out recently by Berke and Hoffmann.[9] From this it was concluded that for a direct second-order reaction of the type shown below there is a repulsive interaction

TABLE 4

Rate parameters for the reaction of $[MnMe(CO)_5]$ with dmad in different solvents at 25.0 ± 0.1 °C [a]

Solvent	$10^4k_1/s^{-1}$	$10^4k_2/dm^3\ mol^{-1}\ s^{-1}$	Dielectric constant [b]
Benzene	0.027 ± 0.02	0.27 ± 0.03	2.3
Diethyl ether	0.17 ± 0.02	0.28 ± 0.02	4.3
Dichloromethane	0.14 ± 0.05	0.57 ± 0.07	9.1
Tetrahydrofuran	11.7 ± 0.05 [c]		7.7
Nitromethane	7.9 ± 0.05 [c]		37.4

[a] $[MnMe(CO)_5] = 0.02 \times 10^{-3}$ mol dm^{-3}. [b] 'Handbook of Chemistry and Physics,' 53rd edn., ed. R. C. Weast, C.R.C. Press, Cleveland, Ohio, p. E-43. [c] Obtained from Figure 3 using the relationship $1/k_{obs.} = k_{-1}/k_1k_3[\text{dmad}] + 1/k_1$.



between the σ orbitals of the migrating methyl ligand and the CO ligand. If the attacking ligand L is a donor ligand (nucleophile) the activation energy for this reaction is so high that it does not compete with the usual two-step mechanism (*i.e.* the k_1 path). If, on the other hand, the incoming ligand is an acceptor (electrophile) with low-lying orbitals which can accept electron density this will stabilize the transition state and lower the activation energy for the direct second-order pathway. This appears to be the situation with the electron-deficient acetylenes, dmad, $EtO_2CC_2CO_2Et$, and $HO_2CC_2CO_2H$ studied in this work. As the electron density of the C≡C bond increases then the k_2 path becomes less important.

It has been shown previously [7] that acetylpentacarbonylmanganese also reacts with dmad at room temperature to form the same adduct (1) with loss of carbon monoxide. The kinetics of this reaction have now been studied by following the evolution of CO, and also by i.r. spectroscopy by following the rate of disappearance of the A_1 band at 2 115 cm^{-1} in the metal–carbonyl region of the spectrum of the acetyl complex, and the rate of appearance of the band at 1 968 cm^{-1} in the spectrum of (1). The reactions followed by i.r. spectroscopy were carried out under pseudo-first-order conditions in diethyl ether at 25 °C. In all cases first-order kinetics were obeyed for up to 65% reaction. The observed rate constants (Table 6) were independent of [dmad] and the value of $k_{obs.}$ represents a true-first-order rate constant. These reactions were carried out in a flask sealed with a serum cap; the CO evolved might inhibit the reaction to some extent, although no levelling off of the kinetic curves was noticed for up to one half-life of the reaction. In the reaction followed by CO evolution the conditions used approached second-order and may account for the observed difference in the rate constants.

TABLE 5

Rate parameters for the reactions of $[MnMe(CO)_5]$ with different acetylenes in diethyl ether at 25.0 ± 0.1 °C

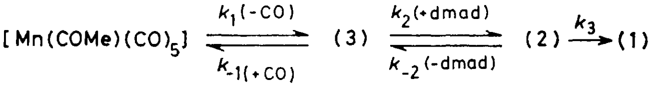
Acetylene	$10^4k_1/s^{-1}$	$10^4k_2/dm^3\ mol^{-1}\ s^{-1}$
$HO_2CC_2CO_2H$	0.11 ± 0.03	2.17 ± 0.14
$EtO_2CC_2CO_2Et$	0.03 ± 0.03	1.09 ± 0.21
$HOCH_2C_2CH_2OH$	0.08 ± 0.05	0.69 ± 0.07
$ClCH_2C_2CH_2Cl$	0.02 ± 0.03	0.30 ± 0.06
$CH_3C_2CH_3$	0.00 ± 0.01	0.01 ± 0.01
PhC_2Ph	0.00 ± 0.00	0.00 ± 0.00

TABLE 6

Rate parameters for the reactions of $[Mn(COMe)(CO)_5]$ with dmad in diethyl ether at 25.0 ± 0.1 °C [a]

$10^3[\text{dmad}]/mol\ dm^{-3}$	$10^4k_1/s^{-1}$
1.19 [b]	0.40 ± 0.04 [c]
1.29	0.15 ± 0.01 [d]
1.62	0.14 ± 0.01 [d]
0.97	0.14 ± 0.01 [e]

[a] Except where otherwise stated, $[Mn(COMe)(CO)_5] = 0.082 \times 10^{-3}$ mol dm^{-3}. [b] $[Mn(COMe)(CO)_5] = 1.09 \times 10^{-3}$ mol dm^{-3}. [c] By measurement of CO evolution. [d] By measurement of disappearance of the band at 2 115 cm^{-1} in the i.r. spectrum of $[Mn(COMe)(CO)_5]$. [e] By measurement of the appearance of an i.r. band at 1 968 cm^{-1} due to formation of (1).



SCHEME 2

A mechanism which would account for the lack of dependence on [dmad] is that shown in Scheme 2, in which the rate-determining step is dissociation of a CO ligand from $[Mn(COMe)(CO)_5]$. Using a steady-state approximation for the concentration of the intermediate (3), and assuming that k_{-2} is small this gives the rate law (vii) which, when $k_2[\text{dmad}] \gg k_{-1}[\text{CO}]$, reduces to

$$-\frac{d[Mn(COMe)(CO)_5]}{dt} = \frac{k_1k_2[Mn(COMe)(CO)_5][\text{dmad}]}{k_{-1}[\text{CO}] + k_2[\text{dmad}]} \quad \text{(vii)}$$

$$\text{rate} = k_1[Mn(COMe)(CO)_5] \quad \text{(viii)}$$

equation (viii). As a further check on the validity of this mechanism the rate of thermal decomposition $[Mn(COMe)(CO)_5]$ in diethyl ether at 26.0 °C was determined by measurement of CO evolution. The first-order rate constant of $(0.35 \pm 0.01) \times 10^{-4}\ s^{-1}$ obtained agrees well with those reported by other workers using 2,2′-diethoxydiethyl ether as solvent at 30.5 °C,[3,10,11] and fully supports the proposed mechanism for the reaction with dmad.

EXPERIMENTAL

The complexes $[MnMe(CO)_5]$ and $[Mn(COMe)(CO)_5]$ were prepared by standard procedures.[12] The methyl complex was purified by repeated sublimation under vacuum, and the acetyl complex by repeated recrystallisation from light petroleum to constant m.p. Benzene, diethyl ether, dichloromethane, tetrahydrofuran, and nitromethane were purified according to established methods,[13] and were degassed with dry nitrogen immediately before use. Dimethyl acetylenedicarboxylate was a commercial sample purified by preparative g.l.c. to >99.8% purity; this acetylene deteriorates on standing, and purity checks were carried out by g.l.c. immediately before each kinetic run. Diethyl acetylenedicarboxylate and 1,4-dichlorobut-2-yne were purified by distillation under an atmosphere of dry nitrogen, and but-2-yne-1,4-diol, acetylenedicarboxylic acid, and diphenylacetylene were recrystallised to constant m.p.

I.r. spectra were recorded on a Perkin-Elmer model 257 grating spectrometer using a solution cell of 0.1-mm pathlength with sodium chloride optics; a 2.5 times scale expansion was used for the metal–carbonyl region.

Kinetic Studies.—(*a*) *Using i.r. spectroscopy.* The rates of the reactions were followed by observing changes in the metal–carbonyl stretching frequency region of the i.r. spectra of the reaction mixtures. Measurement of the spectra of pure $[MnMe(CO)_5]$, $[Mn(COMe)(CO)_5]$, and $[Mn\{Z\text{-}MeO_2CC{=}C(COMe)CO_2Me\}(CO)_4]$ at different solution concentrations showed in each case a linear relationship between the absorbance and concentration in accordance with the Beer-Lambert law.

A ten-fold molar excess or more of acetylene over the manganese complex was used in order to attain pseudo-first-order conditions, and linear first-order plots of $\log_{10}(A_t - A_\infty)$ *versus* time, where A_t is the absorbance at any time and A_∞ is the absorbance at infinite time, were obtained for up to at least 65% reaction. Values of $\Delta H_{obs.}^{\ddagger}$ and $\Delta S_{obs.}^{\ddagger}$ were obtained from the Arrhenius plots of log $k_{obs.}$ ([dmad] constant) *versus* $1/T$. Standard errors of estimation were obtained from a least-squares treatment.

In a typical reaction, a solution of $[MnMe(CO)_5]$ was pipetted into a long-necked reaction tube painted black to exclude light. The tube was then purged with dry nitrogen, sealed with a serum cap, and left in a thermostatted water bath at 25.0 ± 0.1 °C overnight. A standard solution of the acetylene, which had been left to equilibrate in the same bath for at least 1 h, was then injected into the reaction tube. The tube was shaken rapidly to ensure adequate mixing, and samples were withdrawn at intervals and injected into the i.r. cell. In all cases the change in temperature and time-delay before recording the spectra were very small. A similar procedure was employed for the reaction of $[Mn(COMe)(CO)_5]$ with dmad.

(*b*) *By measurement of CO evolution.* The rate of reaction was monitored using the apparatus described by Calderazzo and Cotton.[3] In a typical experiment, a solution of dmad (10 cm³ of a 0.12 mol dm⁻³ solution) in diethyl ether was placed in a flask connected to a constant-pressure gas burette. The manganese complex (0.26 g, 1.09 mmol) was placed in a sample tube inside the flask and the apparatus was flushed out with carbon monoxide. The flask and burette were immersed in water jackets supplied by water at the same temperature from a thermostatted bath. Once the contents of the flask had reached thermal equilibrium the reaction was started by tilting the contents of the sample tube into the solution. The volume of CO was measured at known time intervals and the pressure recorded was corrected for the vapour pressure of the solvent and converted to ‘ standard temperature and pressure ’.

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