Mo(CO)₅Py as an Initiator of Polymerization

C. H. BAMFORD, R. DENYER and G. C. EASTMOND

Department of Inorganic, Physical and Industrial Chemistry, University of Liverpool, England

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In a series of publications we have described the kinetics of free-radical formation from molybdenum carbonyl in association with organic halides in a number of electron-donating solvents. Radical formation involves the displacement of carbon monoxide from the carbonyl by the solvent or vinyl monomer in a rate-determining process giving rise to complexes of the type Mo(CO)₅L (where L represents the solvent or monomer) which then react directly with the halide. This paper describes a study of the behaviour of Mo(CO)₅Py in association with organic halides in methyl methacrylate solution. The results show that Mo(CO)₅Py does not react directly with the halide but first undergoes activation by reaction with monomer, mainly with displacement of pyridine. The relative reactivities of complexes of the type Mo(CO)₅L are discussed.

The mechanism previously proposed to account for the inhibition processes observed in Mo(CO)₆-organic halide systems satisfactorily explains the extensive inhibition observed in the present work.

We have postulated that the first step in the formation of free radicals by molybdenum carbonyl in association with organic halides is the displacement of a molecule of carbon monoxide from the carbonyl by a suitable electron-donating solvent, which may be a polymerizable vinyl monomer^{1,2}. The resulting complex (I) then reacts with the halide (e.g. CCl₄) forming a radical (e.g. $\dot{\text{C}}\text{Cl}_3$) by abstraction of a halogen atom³. Derivatives of molybdenum carbonyl are known which have structures analogous to that of (I); among these is the monopyridine complex Mo(CO)₅Py first prepared by STROHMEIER and GERLACH⁴. It appeared to us that interesting information might be obtained from a study of this compound. First, Mo(CO)₅Py might be expected to react directly with the halide, as does (I), so that the rate of radical formation should not become independent of [halide] at "high" values of the latter. Secondly, if an activation process is required before reaction with the halide, it should be possible to determine the relative rates of scission of pyridine and carbon monoxide. Further, scission of pyridine would lead to intermediates identical in nature with those formed from molybdenum carbonyl, so that close similarity with the latter might be anticipated.

STROHMEIER and HARTMANN⁵ have reported a brief investigation of the polymerization of ethyl

acrylate initiated by Mo(CO)₅Py—CCl₄ and interpret their results in terms of a mechanism essentially similar to that proposed for molybdenum carbonyl, with displacement of pyridine by monomer as the first step. The more detailed kinetic studies reported in this paper show that other processes must also be considered and also allow evaluation of the kinetic parameters for two halides. We have used methyl methacrylate as the monomer, and ethyl trichloroacetate and carbon tetrachloride as halides.

Experimental

1. Materials

Methyl methacrylate was purified as described previously⁶. AnalaR carbon tetrachloride was used without further purification and AnalaR ethyl trichloroacetate was fractionally distilled before use. Azo-bis-isobutyronitrile was recrystallised from ethyl alcohol. Mo(CO)₅Py was prepared according to the method of STROHMEIER and GERLACH⁴.

2. Technique

All experiments were performed in inactive light; the reaction mixtures were thoroughly degassed in the conventional manner. A dilatometric technique was used to determine initial rates of polymerization and a gravimetric technique for studying the effect of carbon monoxide on the reaction. The molybdenum derivative was introduced into the reaction vessel as a solution in

¹ C. H. BAMFORD, R. DENYER, and G. C. EASTMOND, *Trans. Faraday Soc.* **61**, 1459 [1965].

² C. H. BAMFORD, R. DENYER, and G. C. EASTMOND, *Trans. Faraday Soc.* **62**, 688 [1966].

³ C. H. BAMFORD, G. C. EASTMOND, and V. J. ROBINSON, *Trans. Faraday Soc.* **60**, 751 [1964].

⁴ W. STROHMEIER and K. GERLACH, *Chem. Ber.* **93**, 2087 [1960].

⁵ W. STROHMEIER and P. HARTMANN, *Z. Naturforschg.* **19 b**, 882 [1964].

⁶ C. H. BAMFORD and C. A. FINCH, *Proc. Roy. Soc. [London], Ser. A* **268**, 553 [1962].

ether; the solvent was then removed in vacuum. The remaining components were distilled into the tube. Mo(CO)₅Py appears to be unstable in the presence of air when in solution, except with ether as solvent, and the above procedure was devised to avoid decomposition arising from this cause.

Pure carbon monoxide, prepared by the thermal decomposition of molybdenum carbonyl, was admitted to reaction vessels at -80°C , after removing residual traces of carbonyl in a trap cooled to -80°C . Carbon monoxide pressures in the reaction vessels at 40°C were calculated from measurements made at -80°C .

Rates of carbon monoxide evolution were determined by means of a Töpler pump, as described in an earlier paper⁷, for reaction times of 20 min at 40°C .

Number-average molecular weights $\bar{M}_n$ of the polymers were measured viscometrically at 30°C , with dry benzene as solvent. The values of K and α employed were those determined by Fox et al.⁸ for use in the intrinsic viscosity-molecular weight relation

$$[\eta] = K \bar{M}_n^{\alpha} \quad (1)$$

(where $[\eta]$ is the intrinsic viscosity) when applied to polymers prepared under conditions of termination by disproportionation of radicals. To allow for the occurrence of some termination by combination the modified relation

$$[\eta] = K \bar{M}_n^{\alpha} \left\{ \frac{2+y}{2(1+y)} \right\}^{\alpha} \left\{ \frac{1+y(1+\alpha/2)}{1+y} \right\} \quad (2)$$

is necessary. Here y is the ratio of combination to disproportionation; it was taken⁹ as 0.34 at 40°C . Values of $k_p k_t^{-1/2}$ were calculated from the equation

$$\frac{k_p}{k_t^{1/2}} = \frac{1}{[M]} \left\{ \bar{P}_n \omega \frac{2+y}{2(1+y)} \right\}^{1/2}, \quad (3)$$

in which ω is the average rate of polymerization, $\bar{P}_n$ the number average degree of polymerization of the resulting polymer, M represents monomer, and k_p and k_t are the velocity coefficients for propagation and termination, respectively.

Equations (2) and (3) were used when chain transfer and retardation were absent; otherwise (1) was employed in calculating molecular weights.

Results and Discussion

1. Effect of halide (ethyl trichloracetate) concentration

The variation in rate of polymerization with [ethyl trichloracetate] is shown in Fig. 1. The results demonstrate that the rate of polymerization

becomes almost independent of [halide] at high values of the latter, a feature which is common in polymerizations initiated by molybdenum and other metal carbonyls in association with various halide

Fig. 1. Dependence of rate of polymerization of methyl methacrylate on $[\text{CCl}_3\text{COOC}_2\text{H}_5]$ at 40°C , $[\text{Mo}(\text{CO})_5\text{Py}] = 1.16 \times 10^{-4}$ mole l^{-1} . Curve calculated from equations (4), (11) and (12).

des¹⁰. The initial portion of the curve in Fig. 1 is much less steep than that of the corresponding curve¹¹ with Mo(CO)₆ at 80°C . Since the rate of a free-radical polymerization is given by

$$-\frac{d[M]}{dt} = \frac{k_p}{k_t^{1/2}} [M] J^{1/2}, \quad (4)$$

where J is the rate of initiation, the observed dependence of rate on [halide] is inconsistent with a direct rate-determining reaction between Mo(CO)₅Py and halide as the first step in the mechanism of radical formation since, in the absence of inhibition, this would not lead to a limiting rate of polymerization at high [halide]. The complex Mo(CO)₅Py does not, therefore, react with halide directly as do complexes formed by displacement of a molecule of carbon monoxide from Mo(CO)₆ by solvents such as methyl methacrylate, ethyl acetate, acetic anhydride and dioxan^{1,2}. As pointed out in an earlier paper¹⁰, reversible complex-formation between the molybdenum derivative and halide would explain the existence of a limiting rate. This alternative is not acceptable in the case of molybdenum carbonyl and other carbonyls studied and we do not think it desirable to invoke such an interpretation for the present system.

2. Dependence of rate on monomer concentration

Benzene behaves as an inert solvent in polymerizations initiated by molybdenum carbonyl and car-

⁷ C. H. BAMFORD and R. DENYER, *Trans. Faraday Soc.* **62**, 1567 [1966].

⁸ T. J. BOX, J. B. KINSINGER, H. F. MASON, and E. M. SCHEULE, *Polymer* **3**, 71 [1962].

⁹ J. C. BEVINGTON, H. W. MELVILLE, and R. P. TAYLOR, *J. Polymer Sci.* **12**, 449 [1954]; **14**, 463 [1954].

¹⁰ C. H. BAMFORD, *J. Polymer Sci. C* **4**, 1571 [1963].

¹¹ C. H. BAMFORD, F. J. T. FILDES, and W. R. MALTMAN, *Trans. Faraday Soc.* **62**, 2544 [1966].

bon tetrachloride at 80 °C, and was used as an inert solvent in the present work in determining the dependence of rate of polymerization on $[M]$. The results obtained, with $[\text{Mo}(\text{CO})_5\text{Py}] = 1.16 \times 10^{-4}$ mole l^{-1} and ethyl trichloroacetate (0.175 mole l^{-1}) as the halide, show that the overall order in $[M]$ is approximately 1.4 (Fig. 2). Comparison of this

Fig. 2. Rate of polymerization as function of monomer concentration with benzene as diluent; 40 °C. $[\text{Mo}(\text{CO})_5\text{Py}] = 1.16 \times 10^{-4}$ mole l^{-1} . $[\text{CCl}_3\text{COOC}_2\text{H}_5] = 0.175$ mole l^{-1} . Curve calculated from equations (4), (11) and (12).

results with (4) suggests that monomer is involved in the radical-forming processes, and we conclude that $\text{Mo}(\text{CO})_5\text{Py}$ must be activated, prior to reaction with halide, by reaction with monomer. From analogy with our previous work on molybdenum carbonyl¹ we propose that the first step is the displacement of a ligand from $\text{Mo}(\text{CO})_5\text{Py}$ by monomer —

a reaction also postulated by STROHMEIER and HARTMANN⁵ in the thermal polymerization of ethyl acrylate initiated by $\text{Mo}(\text{CO})_5\text{Py}$ and CCl_4 . Additional evidence for (5) as the major primary process is presented later. It may be noted that (I) in (5) is identical with the complex formed by displacement of a molecule of carbon monoxide from molybdenum carbonyl by monomer; this displacement is considered to be the primary process in radical formation in molybdenum carbonyl — organic halide systems. A similarity may therefore be expected between the detailed kinetics of radical formation by $\text{Mo}(\text{CO})_6$ and by $\text{Mo}(\text{CO})_5\text{Py}$, since the same reaction intermediates should be involved. Complex (I) would be expected to react with halide H according to (6).

3. Carbon monoxide evolution

An alternative to (5) which must be considered is the displacement of a molecule of carbon monoxide by monomer. In order to distinguish between these possibilities the rate of evolution of carbon monoxide in bulk monomer was studied both in the presence and absence of halide, with the results shown in Table 1.

$[\text{CCl}_3\text{COOC}_2\text{H}_5]$ [mole l^{-1}]	$10^8 d[\text{CO}]/dt$ [mole $l^{-1} \text{ sec}^{-1}$]	No. of CO molecules liberated per molecule of $\text{Mo}(\text{CO})_5\text{Py}$ decomp.
0	2.9	0.35
0.175	15.3	1.5

Table 1. Rates of carbon monoxide evolution at 40 °C. $[\text{Mo}(\text{CO})_5\text{Py}] = 1.16 \times 10^{-4}$ mole l^{-1} .

(The rates have been corrected to allow for consumption of initiator during the 20 min. reaction period.)

The corresponding rate of initiation calculated from (4, 11, 12) is 10.32×10^{-8} mole $l^{-1} \text{ sec}^{-1}$; on the assumption that one radical is formed per molecule of initiator decomposed this is equal to the rate of decomposition of $\text{Mo}(\text{CO})_5\text{Py}$. In this way the figures in column 3 of Table 1 have been derived. It can be seen that in the absence of halide carbon monoxide is evolved, but at a rate which is only one third the rate of decomposition of the initiator, approximately, while in the presence of halide rather more than one molecule of CO is liberated for each initiating radical formed. These results may be compared with those previously obtained with $\text{Mo}(\text{CO})_6$ as a component of the initiating system¹²; in the absence of halide, one molecule of CO is liberated for every molecule of $\text{Mo}(\text{CO})_6$ decomposed, while in the presence of halide approximately two molecules of CO are evolved. If radical formation occurred only through reactions (5, 6), no carbon monoxide would be evolved in the absence of halide and one mole of CO would be liberated per radical formed in the presence of halide. We are, therefore, led to conclude that, to a small extent, monomer may displace CO from $\text{Mo}(\text{CO})_5\text{Py}$ according to the reaction

¹² C. H. BAMFORD, G. C. EASTMOND, and W. R. MALTMAN, *Trans. Faraday Soc.* **62**, 2531 [1966].

$10^5[\text{Mo}(\text{CO})_5\text{Py}]$ [mole l^{-1}]	[Ethyl trichloro- acetate] [mole l^{-1}]	$[\text{CCl}_4]$ [mole l^{-1}]	CO [mm]	$10^5(-d[M]/dt)$ [mole l^{-1} sec $^{-1}$]	$10^{-2} \bar{P}_n^*$	$10^{-2} \bar{P}_n$	$k_p k_t^{-\frac{1}{2}}$ apparent [mole $^{-\frac{1}{2}} l^{\frac{1}{2}} \text{sec}^{-\frac{1}{2}}$]
3.87	0.175	—	0	9.96	25.94	47.14	0.057
6.20	0.175	—	0	11.15	21.43	42.12	0.055
7.75	0.175	—	0	13.48	18.49	33.84	0.056
11.60	0.175	—	0	17.63	12.34	26.64	0.052
11.60	0.175	—	21.0	13.01	20.70	36.10	0.058
11.60	0.175	—	58.0	8.95	30.90	52.49	0.059
11.60	0.175	—	260.0	3.90	74.80	120.4	0.061
7.75	0.0088	—	0	6.39	28.12	73.5	0.048
7.75	—	0.15	0	8.28	19.05	56.80	0.045

Table 2. Rates and degrees of polymerization with Mo(CO)₅Py under different conditions at 40 °C.

which is followed by

which involves a complex (II) identical with that in (6). However, it must be admitted that the amounts of CO evolved in the absence of halide are very small, and the relevant figure in Table 1 may be inaccurate.

According to either mechanism, in the presence of halide the total rate of evolution of CO should be equal to the rate of initiation. The excess carbon monoxide evolved in the presence of halide (Table 1) is thought to arise from side-reactions, probably involving the products of initiation.

From the carbon monoxide evolution and the observed order in monomer we conclude that radical formation occurs predominantly through (5, 6). This conclusion is in agreement with infra-red studies on Mo(CO)₅Py. COTTON and KRAIHANZEL¹³ found that the C—O stretching frequencies in Mo(CO)₅Py and Mo(CO)₅C₆H₁₁NH₂ are virtually identical, and, since C₆H₁₁NH₂ has no acceptor properties, these workers concluded that the Mo—Py bond has no π -bond character. Thus, the partial negative charge on the molybdenum resulting from electron donation from pyridine is used to strengthen the Mo—CO bonds. The high rates of initiation obtained with Mo(CO)₅Py at 40 °C, a temperature at which Mo(CO)₆ is almost inactive, are in agreement with the displacement of pyridine by monomer as the major process leading to radical formation.

4. Dependence of rate on Mo(CO)₅Py concentration

The dependence of the rate of polymerization of bulk methyl methacrylate at 40 °C on [Mo(CO)₅Py], for $[\text{CCl}_3\text{COOC}_2\text{H}_5] = 0.175$ mole l^{-1} and for

$[\text{CCl}_4] = 0.150$ mole l^{-1} is shown in Fig. 3. At very low concentrations of Mo(CO)₅Py the rate of polymerization is approximately proportional to $[\text{Mo}(\text{CO})_5\text{Py}]^{\frac{1}{2}}$, consistent with a free-radical mechanism as found in related systems. As [Mo(CO)₅Py] is increased, the rate of polymerization becomes steadily less dependent on [Mo(CO)₅Py]; this type of behaviour is a feature of many polymerizations initiated with derivatives of metals in their zero oxidation states in association with organic halides¹⁰, and is indicative of the occurrence of retardation or inhibition by initiator or a derived intermediate.

Table 2 shows the rates and degrees of polymerization observed under various experimental conditions. For comparison, we have calculated 'expected' degrees of polymerization $\bar{P}_n^*$ from the observed rates of polymerization using a value of $k_p k_t^{-\frac{1}{2}} = 0.077$ mole $^{-\frac{1}{2}} l^{\frac{1}{2}} \text{sec}^{-\frac{1}{2}}$ which we have found to hold for the polymerization of methyl methacrylate at 40 °C initiated by azo-bis-isobutyronitrile, in the absence of retardation or transfer.

Consideration of the values of $\bar{P}_n$ and the dependence of rate of polymerization on [Mo(CO)₅Py] shows that at high [Mo(CO)₅Py] both 'low' rates and low values of $k_p k_t^{-\frac{1}{2}}$ are observed experimentally, an effect consistent with retardation. However, it may be seen from $\bar{P}_n$ and $\bar{P}_n^*$ in Table 2 that to explain these results on the basis of retardation there must be approximately one act of retardation for each initiation at low values of [Mo(CO)₅Py] when ethyl trichloroacetate is the halide. This conclusion is not in agreement with the observed proportionality between the rate of polymerization and $[\text{Mo}(\text{CO})_5\text{Py}]^{\frac{1}{2}}$ at low [Mo(CO)₅Py]. Further, in

¹³ F. A. COTTON and C. S. KRAIHANZEL, J. inorg. Chem. **2**, 533 [1963].

order to account for the observed rates of polymerization in terms of retardation, it is necessary to assume a high value of the rate constant of reaction (5), giving a half-life of the initiator of the order of 5 minutes; this is incompatible with experimental dilatometric contraction-time curves which show no evidence of a decrease in rate prior to a reaction time of 9–10 minutes.

In the polymerization of methyl methacrylate initiated by molybdenum carbonyl and carbon tetrachloride relatively low rates of polymerization are observed at high carbonyl concentrations. These reactions have been considered in detail¹² and the low rates are attributed to inhibition arising from interactions between the intermediates in the initiation. The proposed inhibition process involves complexes identical with (I) and (II) formed in (5), (6) and (8) in the present work, which are supposed to undergo a mutual destruction reaction:

An exact correspondence between theory and experiment using (9) was not achieved in the case of molybdenum carbonyl; however, the proposed mechanism does appear to give a fair description of the main inhibition process, although other processes may also be involved. On the basis of reaction (9) inhibition will be more marked in reactions initiated with $\text{Mo}(\text{CO})_5\text{Py}$ at 40 °C; approximately the same rates of polymerization are observed in these reactions as in polymerizations initiated with molybdenum carbonyl at 80 °C, but since $k_p k_t^{-\frac{1}{2}}$ is greater at 80 °C by a factor of two the stationary concentrations of (I) and (II) in the present work will be approximately four times as great as those in the molybdenum carbonyl reactions. Also the decomposition of (II) into radicals is associated with a positive activation energy so that, for a given rate of initiation, the concentration of (II) will be higher at 40 °C. Earlier work¹⁴ on the $\text{Mo}(\text{CO})_6 - \text{CCl}_4$ system at 80 °C has shown there is a tendency for $k_p k_t^{-\frac{1}{2}}$ to decrease with increasing [carbonyl], and this was attributed to retardation by carbonyl. However, the effect may equally well be interpreted on the basis of transfer to an intermediate or product of initiation. The possibility that transfer to pyridine liberated in (5) gives rise to the low values of $k_p k_t^{-\frac{1}{2}}$ is ruled out since we have shown that

pyridine is ineffective as a transfer agent in the polymerization of methyl methacrylate. Transfer must, therefore presumably occur to a molybdenum-containing species, but the nature of the reaction is not clear.

5. Effect of carbon monoxide on the reaction

Table 3 illustrates the effect of added carbon monoxide on the rate of polymerization of bulk methyl methacrylate initiated by $\text{Mo}(\text{CO})_5\text{Py}$ and ethyl trichloroacetate. The reduction in rate with increasing carbon monoxide pressure is similar to

CO pressure [mm]	0	21	58.4	141.1	259.4	567.5
$10^5 (-d[M]/dt)$ mole $l^{-1} \text{sec}^{-1}$	17.63	13.01	8.95	6.13	3.90	3.05

Table 3. Dependence of rates of polymerization at 40 °C on the pressure of added carbon monoxide.

that observed with $\text{Mo}(\text{CO})_6$ ¹⁴, although the sensitivity to CO pressure is slightly less marked in the present case. Kinetic studies on initiation by $\text{Mo}(\text{CO})_6 - \text{CCl}_4$ at 80 °C have shown that CO acts as an inhibitor, reducing the rate of initiation, by reacting with complex (I) to displace monomer and reform $\text{Mo}(\text{CO})_6$. The same reaction may be supposed to occur in $\text{Mo}(\text{CO})_5\text{Py} - \text{CCl}_3\text{COOC}_2\text{H}_5$ systems at 40 °C, the resulting molybdenum carbonyl being inactive in comparison to $\text{Mo}(\text{CO})_5\text{Py}$. A reaction of this type is consistent with the decrease in chain transfer observed in the presence of carbon monoxide (Table 2).

6. Mechanism of initiation

We suggest that radical-formation occurs mainly through the mechanism (10) below, in which the initial step corresponds to reaction (5). If the mechanism (7,8) participates to a significant extent an additional set of similar equations would be required, and the complete kinetic analysis would be extremely cumbersome. Since (7,8) is unlikely to be important we prefer to consider only (10); the velocity coefficients may, as a first approximation, be considered to be composite parameters if reactions (7,8) are significant.

¹⁴ C. H. BAMFORD and C. A. FINCH, *Trans. Faraday Soc.* **59**, 118 [1963].

$$J = \frac{k_4}{k_4 + k_6} \cdot \frac{k_1}{2\Delta} \left(\Delta[\text{C}][\text{M}] + \frac{k_2'}{k_3} + \frac{k_2''[\text{CO}]}{k_3} + [\text{H}] + \frac{k_2[\text{Py}]}{k_3} \right) \times \left[\left\{ 1 + \frac{4\Delta[\text{C}][\text{M}][\text{H}]}{\left(\Delta[\text{C}][\text{M}] + \frac{k_2'}{k_3} + \frac{k_2''[\text{CO}]}{k_3} + [\text{H}] + \frac{k_2[\text{Py}]}{k_3} \right)^2} \right\}^{\frac{1}{2}} - 1 \right] \quad (11)$$

where C represents Mo(CO)₅Py and $\Delta = k_1 k_5 \{k_3(k_4 + k_6)\}^{-1}$. The corresponding rate of polymerization is obtained by substituting J from (11) into (4).

Inspection of (11) shows that, in agreement with Fig. 3, the rate of initiation predicted is not proportional to [Mo(CO)₅Py], except at very low values of the latter, on account of the presence of the inhibition reaction (10 f). The extent of inhibition is directly proportional to the value of Δ ,

Fig. 3. Rate of polymerization of methyl methacrylate as function of initiator concentration; 40 °C. o, [CCl₃COOC₂H₅] = 0.175 mole l⁻¹; Δ, [CCl₄] = 0.150 mole l⁻¹. Curve o calculated from equations (4), (11) and (12). Curve Δ calculated from equations (4), (11) and (13).

which in turn depends on the nature of the halide. Previous work¹² with Mo(CO)₆ has shown that Δ is greater for carbon tetrachloride than for ethyl trichloroacetate. The relatively low rates of polymerization observed in the present work with CCl₄

This mechanism is almost identical with that proposed previously for initiation by Mo(CO)₆ - CCl₄ at 80 °C with the modification that both pyridine and carbon monoxide are considered to deactivate complex (I), and the introduction of (10 g) (see below).

Applying the stationary state hypothesis and assuming that only radicals R_· initiate polymerization, we find that the rate of initiation from (10) is given by

as halide (Fig. 3) cannot be adequately explained solely by increased inhibition, and it is necessary to propose that the CCl₄ system has a reduced efficiency of initiation at 40 °C. Reaction (10 g) has been included to account for the reduced rate of initiation with carbon tetrachloride.

7. Kinetic parameters

(a) Ethyl trichloroacetate

The curves in Figs. 1, 2, 3 have been calculated from equations (4) and (11) with the aid of the numerical values given in (12), and taking $k_p k_t^{-\frac{1}{2}} = 0.077 \text{ mole}^{-\frac{1}{2}} \text{ l}^{\frac{1}{2}} \text{ sec}^{-\frac{1}{2}}$ and [M] = 8.9 mole l⁻¹.

$$\begin{aligned}
 k_1 &= 1.0 \times 10^{-4} \text{ mole}^{-1} \text{ l sec}^{-1}, \\
 k_6 &= 0, \\
 \Delta &= 40 \text{ mole}^{-1} \text{ l}.
 \end{aligned} \quad (12)$$

Since the rates are initial values, [CO] = [Py] = 0. The term k_2'/k_3 in (11) has been omitted; it is likely to be small since ethyl trichloroacetate is a very active halide (i.e. k_3 is large), and comparison with corresponding observations on molybdenum carbonyl¹¹ at 80 °C suggest that $k_2'/k_3 < 10^{-2}$. It is, therefore, small compared to $\Delta[\text{C}][\text{M}]$ in Fig. 1 and to [H] in Figs. 2, 3.

It is interesting to note that the small deviation from 1.5 in the observed order in monomer is capable of explanation in terms of inhibition alone, as in the above treatment. The belief that benzene behaves as an inert solvent in these systems is, therefore, retained.

(b) Carbon tetrachloride

The parameters given in (13) are found to give the best agreement with the experimental results of Fig. 2.

$$\begin{aligned} k_1 &= 1.0 \times 10^{-4} \text{ mole}^{-1} \text{ l sec}^{-1}, \\ k_2'/k_3 &= 0.1 \text{ mole l}^{-1}, \\ k_6/k_4 &= 0.72, \\ \Delta &= 80 \text{ mole}^{-1} \text{ l}. \end{aligned} \quad (13)$$

The value of Δ reflects the increased inhibition in systems containing carbon tetrachloride. On account of the lower activity of CCl₄, k_2'/k_3 cannot be neglected; the value in (13) is consistent with that derived¹ at 80 °C for Mo(CO)₆. The existence of reaction (10 g) has not previously been considered in Mo(CO)₆ systems, and to be consistent with earlier work¹² $k_6/k_4 \gtrsim 1/9$ at 90 °C. If we take $k_6/k_4 = 1/9$, comparison with (13) shows that the difference in the activation energies of (10 e, g) is 8.5 k.cal, approximately; this appears to be a reasonable value.

Conclusions

Under the experimental conditions employed the compound Mo(CO)₅Py does not appear to react directly with organic halides, but requires preliminary activation by reaction with monomer. Clearly the complexes postulated in previous work^{1,2} i.e. Mo(CO)₅L where L = methyl methacrylate, ethyl acetate, dioxan, acetic anhydride, are more reactive than Mo(CO)₅Py; this is in keeping with the fact that they have not been isolated. The case in which L = benzonitrile² is a borderline one; although the complex does not seem to have been isolated, acti-

vation is required before reaction with CCl₄ is possible. The relatively stable complexes in which the ligands are phosphine derivatives also require activation¹¹. The reactivities of complexes of the type Mo(CO)₅L considered in this and preceding studies follow the order

O-compound > nitrile > N-base > P-compound > CO. This agrees with the views of STROHMEIER¹⁵ who proposed the reverse order for the stability of the complexes. Although the replacement of a molecule of carbon monoxide by a purely donating ligand strengthens the remaining Mo—CO bonds through increased back-donation it is evident that the resulting complex is more reactive and less stable.

The value of k_1 for Mo(CO)₆ at 40 °C, extrapolated from results at higher temperatures is approximately $5 \times 10^{-8} \text{ mole}^{-1} \text{ l sec}^{-1}$; thus, according to (13), Mo(CO)₅Py is approximately 2000 times more active than Mo(CO)₆ at 40 °C.

The primary displacement of pyridine has also been suggested by STROHMEIER and HARTMANN⁵. Although this may be the main activation process, the idea that radical-forming reactions may occur to some extent after displacement of CO is supported by the work of GRAHAM and ANGELICI¹⁶, who inferred from infra-red evidence that complexes of the types Mo(CO)₅L, Mo(CO)₄L₂, Mo(CO)₄PyL result from reactions between Mo(CO)₅Py and various phosphorus-containing ligands.

There is large amount of inhibition in polymerizations initiated by Mo(CO)₅Py; this would be anticipated from earlier studies on molybdenum carbonyl at 80 °C, since similar intermediates are involved, and the concentrations are such as to favour inhibition at 40 °C. The same quantitative treatment applies in both systems.

¹⁵ W. STROHMEIER, *Angew. Chem. Internat. Edit.* **3**, 730 [1964].

¹⁶ J. R. GRAHAM and R. J. ANGELICI, *J. Amer. chem. Soc.* **87**, 5590 [1965].