A Chain Process in the Oxidation of Molybdenum Carbonyl by Carbon Tetrabromide

By C. H. BAMFORD, G. C. EASTMOND, and F. J. T. FILDES

(*Department of Inorganic, Physical and Industrial Chemistry, Donnan Laboratories, University of Liverpool, Grove Street, P.O. Box* 147, *Liverpool* L69 3BX)

Summary The oxidation of $\mathrm{Mo(CO)_6}$ by $\mathrm{CBr_4}$ in ethyl acetate at 80° can proceed rapidly by a chain process which is strongly inhibited by olefinic additives: it is suggested that the chain carriers are $\dot{\mathrm{C}}\mathrm{Br_3}$ radicals.

THE initial step in the thermal reaction between $\mathrm{Mo(CO)_6}$ and $\mathrm{CCl_4}$ in the presence of a donor solvent ds is the ligand exchange (1) leading to $\mathrm{Mo(CO)_5ds}$; the latter is then oxidised by the halide to a derivative of $\mathrm{Mo^I}$ with formation of $\dot{\mathrm{C}}\mathrm{Cl_3}$ radicals (2; X = Cl).[1-3]

$$\mathrm{Mo(CO)_6 + ds \rightarrow Mo(CO)_5(ds) + CO} \tag{1}$$

$$\mathrm{Mo(CO)_5(ds) + CX_4 \rightarrow Mo^I + \dot{C}X_3} \tag{2}$$

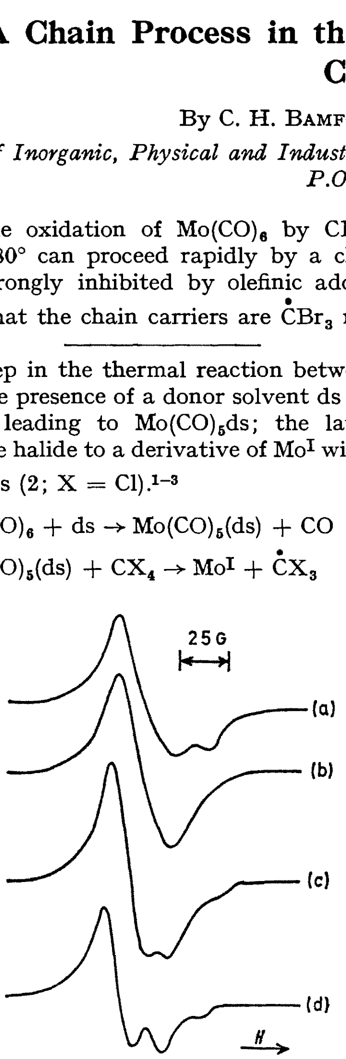

FIGURE 1. *E.s.r. spectra (room temperature) of paramagnetic products formed in the reaction between* $\mathrm{Mo(CO)_6}$ *and* $\mathrm{CBr_4}$ *in ethyl acetate at* 80°. $[\mathrm{Mo(CO)_6}] = 7{\cdot}0 \times 10^{-5}\,\mathrm{M}$; $[\mathrm{CBr_4}] = 0{\cdot}192\,\mathrm{M}$. *Reaction times*: (a) 0·25, (b) 1·5, (c) 6, (d) 48 h.

Secondary, relatively slow, oxidation of the $\mathrm{Mo^I}$ species produces a derivative of $\mathrm{Mo^V}$, which possesses one unpaired electron per molybdenum atom and has a characteristic e.s.r. spectrum.[4] In the early stages of reaction the e.s.r. signal therefore develops at a rate which is considerably lower than that corresponding to the rate of radical formation. We now show that different phenomena are encountered when the halide is $\mathrm{CBr_4}$, and that under suitable conditions, the oxidation of $\mathrm{Mo(CO)_6}$ has the characteristics of a chain process.

E.s.r. spectra of the paramagnetic species formed at various stages of the reaction between $\mathrm{Mo(CO)_6}$ and $\mathrm{CBr_4}$ in EtOAc at 80° are shown in Figure 1. It appears that more than one (and probably three) species containing $\mathrm{Mo^V}$ are formed, the relative concentrations depending on the extent of reaction. The doubly-integrated signal intensity, which is a measure of the total number of unpaired spins, is shown as a function of time in Figure 2 for $[\mathrm{CBr_4}] = 0{\cdot}192$ M and three initial values of $[\mathrm{Mo(CO)_6}]$. Conversion into paramagnetic products is virtually complete after 1—2 hr., the maximum concentration corresponding to one spin per molybdenum atom. The time for half conversion is approximately 0·25 hr. The first order constant for the decay of $\mathrm{Mo(CO)_6}$ by reaction (1) in ethyl acetate at 80° is $1{\cdot}0 \times 10^{-4}\,\mathrm{sec.}^{-1}$, corresponding to a half-life of 1·93 hr.[1] Clearly in the present experiments (1) is not the only process by which the carbonyl is consumed.

Much lower rates of development of signal intensity are found when the reaction is carried out in the presence of 10% (v/v) of methyl methacrylate or cyclohexene, or when methyl methacrylate is the solvent. Indeed, the half-life in these circumstances approximates to that determined by reaction (1). Since these unsaturated compounds are most likely to act as free-radical scavengers, it follows that radicals formed by (2; X = Br) are probably involved in the reactions leading to the rapid decay of $\mathrm{Mo(CO)_6}$.

Tracer experiments with $^{14}CBr_4$ have identified the primary radicals in the thermal polymerization of methyl methacrylate initiated by $Mo(CO)_6$ and CBr_4 as $\dot{C}Br_3$.

We have demonstrated the occurrence of a reaction between $Mo(CO)_6$ and $\dot{C}Br_3$ radicals by utilising the photoreaction ($\lambda = 4358$ Å) between manganese carbonyl and CBr_4, which has been shown by polymerization studies[5] to yield $\dot{C}Br_3$. When a mixture of $Mo(CO)_6$ ($3{\cdot}79 \times 10^{-4}$M), $Mn_2(CO)_{10}$ ($2{\cdot}57 \times 10^{-4}$M) and CBr_4 (0·2 M) in ethyl acetate solution is irradiated at 25° and 4358 Å, paramagnetic species having an e.s.r. spectrum like those in Figure 1 are formed. The spectrum increases in intensity with the period of irradiation, but does not change in the dark. No e.s.r. signal is obtained if 10% (v/v) of methyl methacrylate is added before illumination. Irradiation of solutions of the separate carbonyls in EtOH containing CBr_4 does not give any product with a detectable e.s.r. spectrum.

We suggest that the reaction between $Mo(CO)_6$ and $\dot{C}Br_3$ follows equation (3)

$$Mo(CO)_6 + \dot{C}Br_3 \rightarrow Mo^I + CBr_2. \qquad (3)$$

Polymerization studies have indicated that during the oxidation of Mo^I to Mo^V by CBr_4, $\dot{C}Br_3$ radicals are formed.[6] This process is represented by the non-stoicheiometric equation (4), in which n is the number of radicals generated in the secondary oxidation per molybdenum atom.

$$Mo^I + CBr_4 \rightarrow Mo^V + n\dot{C}Br_3 \qquad (4)$$

In the absence of radical scavengers (3), (4) constitute a chain process; the chains are initiated by $\dot{C}Br_3$ formed in the conventional mechanism (1), (2) (X = Br). Since, in the presence of methyl methacrylate or cyclohexene, the rate of development of the e.s.r. signal appears to be determined by the rate of (1), reaction (4) must be relatively rapid (for $[CBr_4] = 0{\cdot}2$ M). Reactions (3), (4) can thus lead to the rapid oxidation of $Mo(CO)_6$ by a route which bypasses the normal reaction mechanism controlled by (1). At lower concentrations of CBr_4 (3×10^{-3} M) (4) occurs only slowly, and the chain oxidation does not result in a rapid consumption of $Mo(CO)_6$.

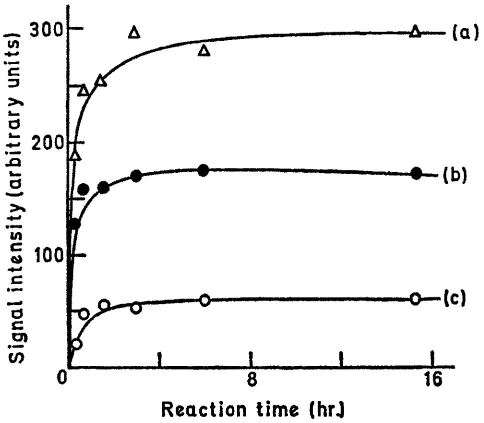

FIGURE 2. *Development of the room temperature e.s.r. signal with reaction time at 80° in the system* $Mo(CO)_6$–CBr_4–EtOAc. (a) $[Mo(CO)_6] = 3{\cdot}5 \times 10^{-4}$M; (b) $[Mo(CO)_6] = 2{\cdot}1 \times 10^{-4}$M; (c) $[Mo(CO)_6] = 7{\cdot}0 \times 10^{-5}$M; $[CBr_4] = 0{\cdot}192$M.

The observations described are not consistent with a rapid direct reaction between $Mo(CO)_6$ and CBr_4, since this would not be inhibited by the presence of unsaturated molecules.

(*Received, November 27th,* 1969; *Com.* 1799.)

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[5] F. J. T. Fildes, unpublished observations.
[6] C. H. Bamford, G. C. Eastmond, and F. J. T. Fildes, in course of publication.