Oxidation of Molybdenum Carbonyl and Related Derivatives by Organic Halides; Thermal and Photochemical Activation

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Summary The thermal reaction between $Mo(CO)_6$ and CCl_4 in ethyl acetate solution at 80° involves intermediate formation of $Mo(CO)_5EtOAc$ (I), which is successively oxidised to Mo^I and Mo^V derivatives, the step $Mo^0 \rightarrow Mo^I$ being mainly responsible for free-radical formation: (I) prepared photochemically reacts similarly with CBr_4 at room temperature.

IT is well-established that under suitable conditions molybdenum carbonyl is oxidised by certain halogen compounds (*e.g.* CCl_4, CCl_3CO_2Et) with production of free radicals (*e.g.* $\dot{C}Cl_3$, $\dot{C}Cl_2CO_2Et$) which are capable of initiating the polymerization of vinyl monomers.[1–5] This interaction does not occur directly between the two species, but requires preliminary activation of the carbonyl, for example by ligand replacement. We have already reported[3] that a paramagnetic molybdenum product is formed which exhibits a characteristic e.s.r. spectrum. In this communication we consider the nature of the reaction products and the mechanism of their formation by thermal or photochemical activation.

The e.s.r. spectrum obtained from $Mo(CO)_6$ and CCl_4 or CCl_3CO_2Et in ethyl acetate solution at 80° is shown in Figure 1. Under the conditions specified, the spectrum is detectable after 0·25 hr. and its intensity increases with reaction time, finally attaining a constant value. It consists of a strong central line at $g = 1{\cdot}947$ together with six satellites with intensities corresponding to the known abundancies of the ^{95}Mo and ^{97}Mo isotopes. Absolute spin concentrations were determined by comparison with solutions of αα-diphenyl-β-picrylhydrazyl and $MoCl_5$; the maximum signal intensity was thus shown to correspond to one unpaired electron per molybdenum atom in the final product, which is therefore almost certainly a derivative of Mo^I or Mo^V. The spectrum in Figure 1 is, in fact, qualitatively similar to spectra of Mo^V derivatives previously reported,[6] but differs from the single example of a Mo^I spectrum available in the literature.[7] Thus these observations suggest that our molybdenum product is a derivative of Mo^V. This view is supported by kinetic evidence derived from a comparison of polymerization and e.s.r. studies, which shows that the rate of development of the e.s.r. signal is less than would be expected if Mo^I were the final product. A detailed account of the kinetic work will be published subsequently.

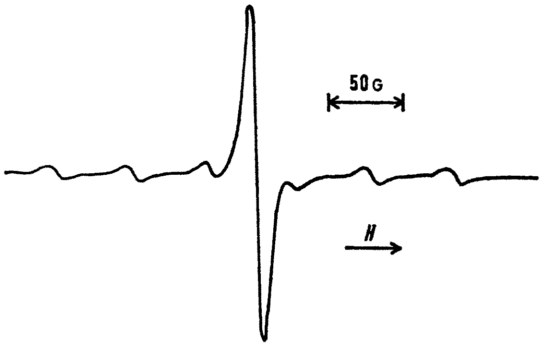

FIGURE 1. *E.s.r. spectrum (room temperature) of paramagnetic products formed in the reaction between* $Mo(CO)_6$ *and* CCl_4 *or* CCl_3CO_2Et in EtOAc *at* 80°. $[Mo(CO)_6] = 3{\cdot}5 \times 10^{-4}$M; [halide] = 0·192M.

We infer from the experiments described that derivatives of molybdenum in oxidation states below five might be readily oxidised by organic halides. To examine this possibility we synthesized $[Mo^I(CO)_2(diphos)_2]I_3$[8] [diphos ≡ $(-CH_2PPh_2)_2$] and $Mo^{III}I_3$[9] and examined their reactions with CCl_4. In view of the paucity of published e.s.r. data on Mo^I compounds we reproduce in Figure 2 the e.s.r. spectra of the former in EtOAc–Me_2CO mixtures, taken at room temperatures and at 77° K. The room temperature spectrum may be interpreted in terms of the interaction of the unpaired electron with four ^{31}P atoms of nuclear spin ½; a small distortion of the spectrum at low field is present, the origin of which has not been determined. The spectrum of MoI_3 in tetrahydrofuran was poorly defined and consisted of a very broad line several hundred gauss wide, with no detectable fine structure. On heating these model compounds to 80° in the presence of CCl_4 the e.s.r. spectra rapidly changed to a spectrum identical with that in Figure 1; this behaviour is clearly consistent with the view that both reactions, like the $Mo(CO)_6$–CCl_4 reaction, lead to Mo^V.

We have shown previously[3–5] that in systems in which $Mo(CO)_6$ + halide is used as an initiator of polymerization the activating ligand replacement forms the species $Mo(CO)_5(ds)$, (where ds is a donor solvent, or the monomer) which is subsequently oxidised by the halide. Strohmeier and Gerlach,[10] Dobson *et al.*[11] and Dobson[12] have demonstrated that an identical species is formed by photolysis of $Mo(CO)_6$ in donor solvents, and it was of obvious interest to examine the behaviour of these products in the presence of halides.

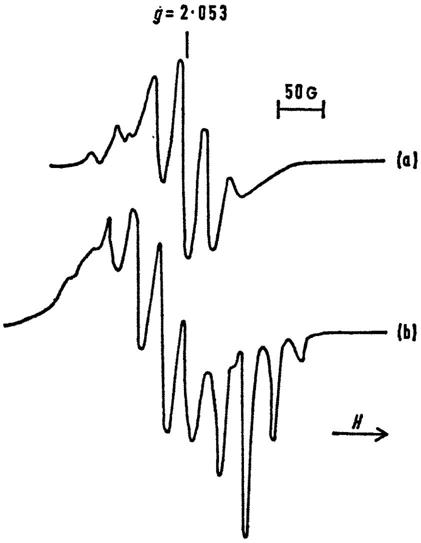

FIGURE 2. *E.s.r. spectra of* $[Mo^I(CO)_2(diphos)_2]I_3$ *in* 4:1 (v/v) *ethyl acetate:acetone:* $[\{Mo^I(CO)_2(diphos)_2\}I_3] = 1{\cdot}45 \times 10^{-4}$M. (a) *Room temperature*; (b) 77° K.

After irradiation of $Mo(CO)_6$ in EtOAc solution in the absence of air by the full light of a medium pressure quartz mercury arc (250w ME/D) CBr_4 was added to give $[CBr_4]$ = 0·15 M, approximately. The characteristic e.s.r. spectrum was found to develop slowly on standing in the dark at 25°. No spectrum could be detected in a blank experiment without irradiation. We have also demonstrated that free radicals are formed when CBr_4 is added to a previously irradiated solution of $Mo(CO)_6$. In this experiment the halide was added as a solution in methyl methacrylate, in the absence of air. After standing for 2¼ hr. in the dark at 25°, the solution was poured into an excess of methanol and the precipitated polymer dried and weighed. For an initial carbonyl concentration of $3{\cdot}79 \times 10^{-3}$ M and a monomer concentration of 6·6 M the mean rate of polymerization over the 2¼ hr. period was found to be $4{\cdot}58 \times 10^{-5}$ M sec.$^{-1}$. The thermal rate of polymerization, in the absence of irradiation, is negligible in comparison.

Reactions of the model Mo^I and Mo^{III} derivatives with

CCl_4, while producing Mo^V, do not yield radicals capable of initiating polymerization. On the other hand, experiments which will be described in a later paper[13] show that in the $Mo(CO)_6$–CCl_4 system, secondary oxidations of the above type do lead to radical formation. However, these processes are relatively slow, so that for short reaction times, such as those employed in kinetic studies on the initiation of polymerization, effectively all the initiating radicals arise from the oxidation of the carbonyl to the Mo^I derivative. This conclusion supports ideas previously developed.[1,3–5]

(*Received, November 27th,* 1969; *Com.* 1798.)

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