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Photolysis of $Mn_2(CO)_{10}$ in the Presence of a Polymeric Ligand

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The study of the photolysis of $Mn_2(CO)_{10}$(1) in various solvents has been the subject of several papers [1]. In particular definitive evidence has been given that the room temperature photolysis of such complex in THF leads to a paramagnetic Mn(II) species through the reaction:

$$3\,Mn_2(CO)_{10} + 12\,S \xrightarrow{h\nu} 2\,Mn(S)_6^{2+} + 4\,Mn(CO)_5^- + 10\,CO$$

(S = solvent)

An extensive study [2a] of this reaction at various temperatures and solvents has been carried out and showed the possibility of obtaining several species, all in agreement with the above reaction. In particular it has been assumed that formation of ion pairs takes place between the two manganese species originated in the disproportionation, that is $Mn(S)_6^{2+}$ and $Mn(CO)_5^-$ (3). This hypothesis has been confirmed by an IR investigation on the same system [2b].

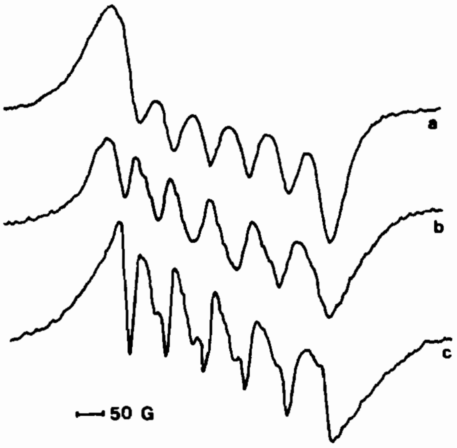


Fig. 1. ESR spectra of solutions of $Mn_2(CO)_{10}$–THF with 4-picoline. (a) Spectrum irradiated at 293 K and registered at r.t. (b) Spectrum irradiated at 293 K and registered at 140 K. (c) Spectrum irradiated at 250 K and registered at 140 K.

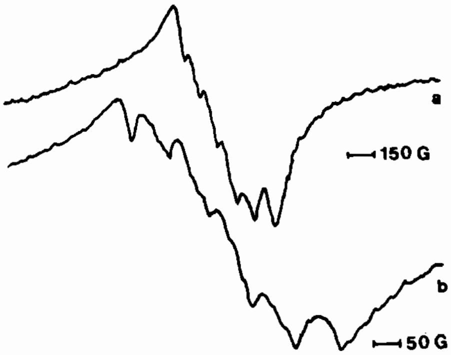


Fig. 2. ESR spectrum at 140 K of the slurry of $Mn_2(CO)_{10}$–THF with PVP irradiated at 250 and 293 K (two different scales).

By irradiation at $\lambda > 320$ nm of degassed solutions of $Mn_2(CO)_{10}$ in anhydrous THF at 240 and 293 K respectively, we have obtained the same species, as evidenced by the ESR spectra. However, the species with g = 2.005 and A_{Mn} = 93 gauss (3) is stable only below 250 K, whereas at room temperature a signal with the same g value, but without hyperfine structure is observed. When 4-picoline is added to the system, the ESR spectra obtained from the irradiated solution are reported in Fig. 1. As can be seen irradiation at room temperature at the same wavelength in the presence of the nitrogen donor ligand produces a species with a different hyperfine structure in comparison with the one observed in the absence of the ligand (A_{Mn} = 87 gauss). At low temperature the species already detected in THF is predominantly obtained.

When finely ground poly-vinylpiridine (PVP) [3] is suspended in the THF solution and the resulting slurry is irradiated, independently of the temperature, a paramagnetic species is observed which is analogous to the one obtained with 4-picoline at room temperature, but superimposed to a broadened signal probably due to the solution (Fig. 2).

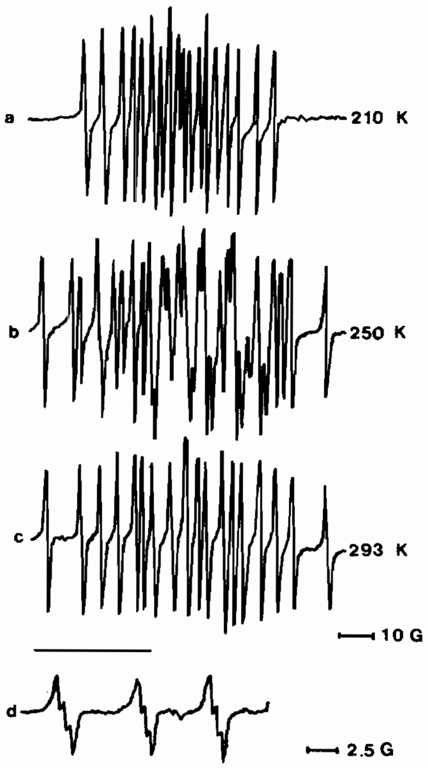
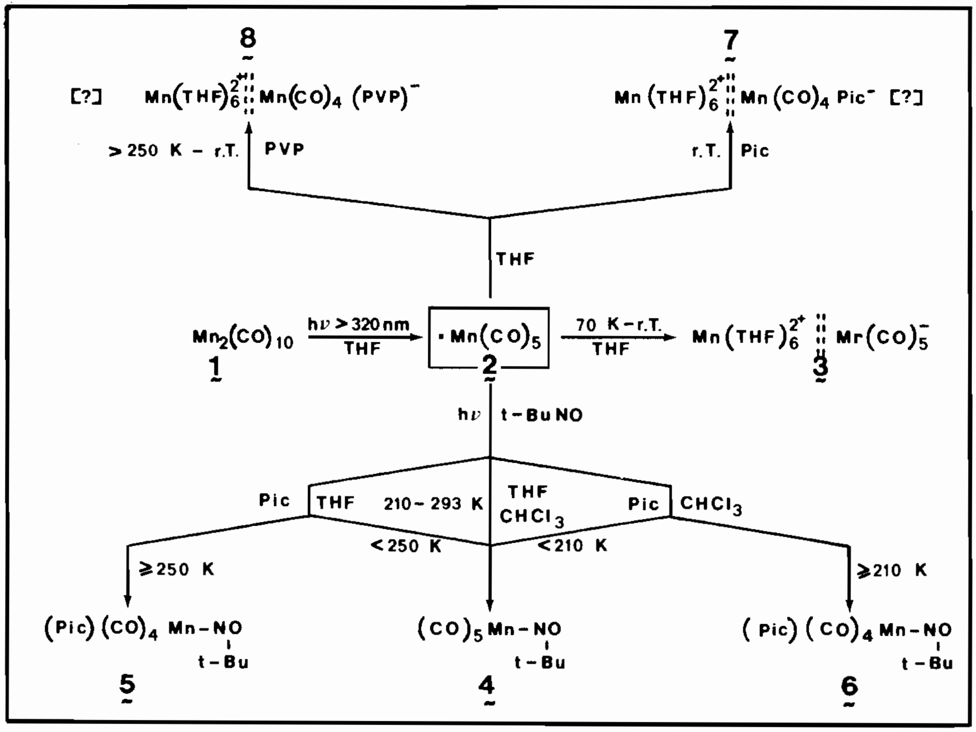


Fig. 3. ESR spectra of $Mn_2(CO)_{10}$–THF with 4-picoline in the presence of t-BuNO. Irradiation temperatures: (a) 210 K; (b) 250 K; (c) 293 K. (d) Spectrum as (c) relative to three lines on an expanded scale ($CHCl_3$ solution).

These results have been checked by adding the radical trap t-BuNO to the system with 4-picoline. As can be seen from Fig. 3 at 210 K the same spectrum as in THF (A_{Mn} = 6.9 gauss, A_N = 16 gauss) [4] (4) is observed. On raising the temperature to 250 K, however, a new signal appears with A_{Mn} = 11.3 gauss and A_N = 17.2 gauss (5) and this is the only one present at room temperature; this latter species is the only one formed when the system is irradiated directly at room temperature. Each line relative to the interaction of the electron with the manganese nucleus is further split by interaction with the picoline nitrogen A_{N_p} = 0.3 gauss). The influence of the picoline nitrogen is better evidenced in chloroform (Fig. 3) (6) where the interaction is already evident at 210 K.

Benner [5] already observed the entry of pyridine into the coordination sphere of manganese by the use of t-BuNO, but she started from partially substituted metal carbonyls. Our results are shown in Scheme I. It is possible to carry out the monosubstitution of CO with nitrogen donor ligands: in homogeneous phase this happens only during irradiation, possibly on a monomeric species. For each system a critical temperature exists below which the substitution does not take place. The species obtained at room temperature when 4-picoline is added (7) is analogous to the one originated with PVP at the two temperatures examined (8). Because all the ESR spectra observed so far can be attributed to manganese ions with an



SCHEME 1

essentially cubic symmetry, we could explain our results on the assumption either that six picoline molecules surround the Mn^{2+} ion, or that substitution involves only the anion $Mn(CO)_5^-$. We discard the first hypothesis on the basis of two facts: when we operate in the presence of t-BuNO we evidentiate a coupling constant for one picoline nitrogen; in addition, in the case of PVP, it is highly reasonable to exclude the coordination of a single ion with six pyridine residues. Therefore we can rationalize our results by the assumption that the substitution is localized on the anion $Mn(CO)_5^-$ forming an ion pair with $Mn(S)_6^{2+}$. The possibility for an outer-sphere ligand to modify appreciably the coupling constant of $Mn(H_2O)_6^{2+}$ has already been proved [6]. Our experiments with PVP show that the substitution of CO with the polymeric ligand is favoured since it manifests itself at a lower temperature than with 4-picoline. In addition PVP has a stabilizing effect on the substituted species which appears to be indefinitely stable at room temperature.

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