

Effect of Nitrogen-Donor Ligands on the Stability of the Photolysis Products of $\text{Mn}_2(\text{CO})_{10}$

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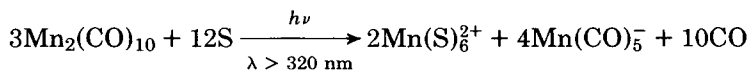
Synopsis

The photolysis of $\text{Mn}_2(\text{CO})_{10}$ in the presence of nitrogen donor ligands has been investigated in various solvents. The disproportionation reaction has been found to be strongly dependent on the solvent and on the temperature. The substitution of CO with the nitrogen donor ligand takes place on the anion $\text{Mn}(\text{CO})_5^-$. The polymeric ligand poly(4-vinylpyridine) manifests a stabilizing effect on the substitution product.

INTRODUCTION

The production of coordinative vacancies in mononuclear fragments obtained by cleavage of the Me-Me bond in metal carbonyls has suggested an investigation of their potential catalytic properties, in particular toward ligands of the olefinic type.¹ A study by Gray and Rembaum² on dicobalt octacarbonyl has significantly confirmed this possibility: actually the olefin hydroformylation reaction catalyzed by $\text{Co}_2(\text{CO})_8$ has been found to differ considerably from the dark reaction when carried out under irradiation at 254 nm, mainly for the extremely bland conditions employed—room temperature and a lower than 1 atm total pressure. In these conditions, however, the reaction is stoichiometric with respect to the cobalt complex. The presence of the polymeric ligand poly(4-vinylpyridine) again confers on the reaction a catalytic character. The same authors assume that irradiation of $\text{Co}_2(\text{CO})_8$ eventually gives rise to carbonyl vacancies in monomeric species linked to the polymer through the pyridine residues. We have undertaken a mechanistic analysis of this photoreaction starting from the analogous dimanganese decacarbonyl complex. The photochemical behavior of $\text{Mn}_2(\text{CO})_{10}$ has been thoroughly investigated.³

According to several authors, the first step of the photoreaction consists in the homolytic cleavage of the Mn-Mn bond, followed by formation of the paramagnetic $\text{Mn}(\text{CO})_5$ monomer, although the real nature of the final products is still matter of debate.^{4,5} In particular, based upon a spectroscopic analysis of the photolytic reaction of $\text{Mn}_2(\text{CO})_{10}$ in THF, the conclusion has been reached by Lappert⁵ that $\text{Mn}(\text{CO})_5$ undergoes a disproportionation reaction at room temperature which yields Mn^{2+} and $\text{Mn}(\text{CO})_5^-$ according to the following scheme:



where S = THF. A more comprehensive analysis carried out by Simpson⁶ on

the same system at several temperatures with different solvents has clearly proved the possibility of obtaining a number of species, all of them in agreement with the scheme shown above. In addition, Simpson has also suggested that "ion pairs" are formed by the two manganese centers $\text{Mn}(\text{S})_6^{2+}$ and $\text{Mn}(\text{CO})_5^-$.

In a short paper⁷ we have reported some preliminary results of an ESR study concerning the photolysis of $\text{Mn}_2(\text{CO})_{10}$ in THF in the presence of nitrogen-donor monomeric and polymeric ligands. On the basis of this study the hypothesis of a replacement by the ligand on the $\text{Mn}(\text{CO})_5^-$ anion appeared justified. This work deals with a more extensive investigation of the monomeric species produced by photolysis in various solvents, carried out by means of IR and ESR techniques.

EXPERIMENTAL

ESR spectra were recorded on a V4500 Varian spectrometer working in the X band. Temperature of recording was controlled by the use of the accessory provided with the instrument. IR spectra were recorded with a Perkin-Elmer 157 spectrophotometer. Spectra of dissolved species were obtained by the use of cells having 100- μm optical paths corrected for the solvent.

The $\text{Mn}_2(\text{CO})_{10}$ was purchased from Fluka and sublimated prior to use.

Photolysis tests were performed under controlled atmosphere of anhydrous nitrogen in a double-window quartz reactor provided with a cooling jacket.

A high-pressure Hg lamp whose UV radiation component was filtered off with a cutoff UV35 filter was used as radiation source.

Solutions of concentration up to $5 \times 10^{-3} M$ were prepared by degassing the solvent through freezing and subsequently distilling it on previously sublimed manganese decacarbonyl. γ -Picoline (Merck) was added to the $\text{Mn}_2(\text{CO})_{10}$ solution in a 1:3 ratio with respect to the solvent by distillation following proper degassing.

PVP produced by Poliscience was added to the complex solution and kept in suspension during the photolytic reaction by stirring the liquid with a magnetic stirrer. Its concentration corresponds to 500 mg per 50 ml solution. The experiments were carried out at 240 and 293 K. Samples for ESR and IR spectroscopic measurements were withdrawn from the reaction vessel under nitrogen. Final products were isolated by solvent evaporation under reduced pressure. Solid residues were repeatedly washed with petroleum ether. PVP was isolated by filtration under nitrogen and repeatedly washed with the reaction solvent.

Finally, $\text{NaMn}(\text{CO})_5$ was synthesized according to the literature.⁸

RESULTS

Photolysis of $\text{Mn}_2(\text{CO})_{10}$

When performed in THF at room temperature, photolysis tests carried out for as long as 6 hr have not offered any evidence of the formation of new species with both ESR and IR spectroscopic techniques. In particular, ESR did not show any signal corresponding to paramagnetic species, while the IR spectrum of manganese decacarbonyl remained clearly unchanged. An analogous absence of ESR signals has been noticed also in the presence of *t*-BuNO.

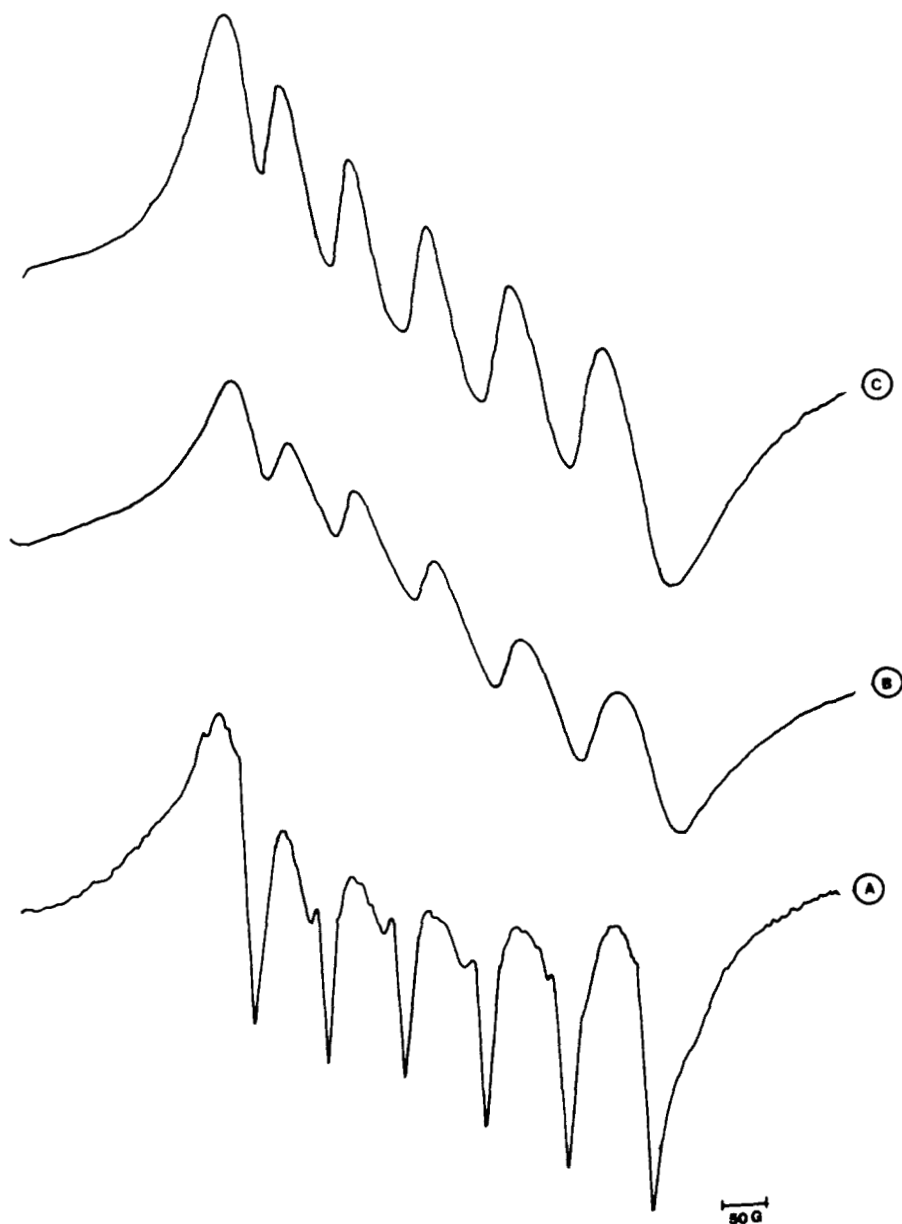


Fig. 1. ESR spectra of irradiated solution of $\text{Mn}_2\text{CO}_{10}$: (a) irradiation temperature, 240 K; registration temperature, liquid N_2 ; solvent, pure THF; (b) irradiation temperature, 293 K; registration temperature, liquid N_2 ; solvent, THF with suspended PVP; (c) irradiation temperature, 293 K; registration temperature, liquid N_2 , solvent, THF- γ -picoline (3:1).

Conversely, at 240 K an ESR signal due to the Mn^{2+} ion with cubic symmetry ($g = 2.005$; $A_{\text{Mn}} = 93$ gauss), see Figure 1(a), has been observed.⁵ However, the IR spectrum remains to a large extent unchanged, even after long irradiation periods, and the characteristic 1894 and 1861 cm^{-1} bands of $\text{Mn}(\text{CO})_5^-$ appear with rather low intensities (Fig. 2).^{9,10} The partial evolution of the system at this temperature has been confirmed by photolysis tests carried out in the

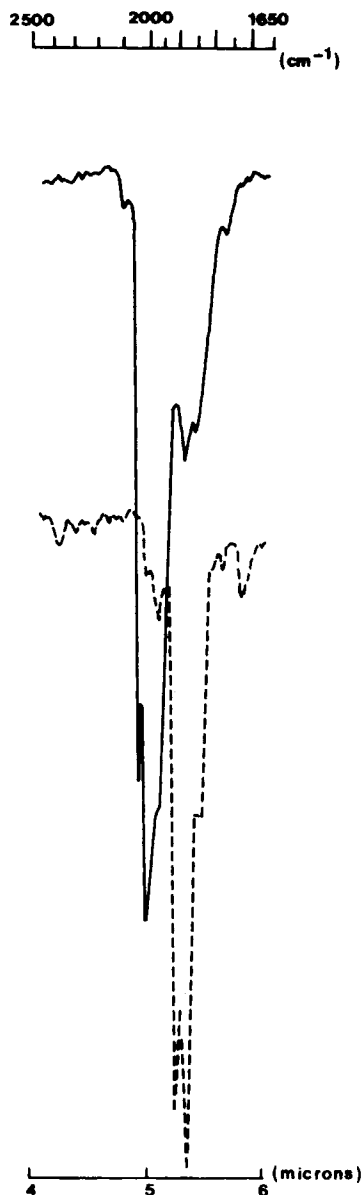


Fig. 2. (—) IR spectrum of an irradiated solution of $\text{Mn}_2\text{CO}_{10}$ in THF at 240 K; (---) IR spectrum to a THF solution of NaMnCO_5 .

presence of *t*-BuNO, which stabilizes the monomeric $\text{Mn}(\text{CO})_5$ species.^{7,11}

IR spectra obtained in acetonitrile are analogous to those measured in THF. ESR measurements at room temperature again show absence of signals, while at low temperature a signal centered about the same *g* value with respect to THF, although lacking the hyperfine structure, was observed. In chloroform, at both temperatures, the IR spectrum shows disappearance of $\text{Mn}_2(\text{CO})_{10}$ but does not offer any evidence of the formation of new carbonyl species. The corresponding ESR spectra are characterized by a broad signal centered at $g \simeq 2$, analogous to that observed by Simpson.⁶

Photolysis of $\text{Mn}_2(\text{CO})_{10}$ in the Presence of γ -Picoline

At room temperature the IR spectrum of the irradiated $\text{Mn}_2(\text{CO})_{10}$ solution in THF containing γ -picoline indicates complete evolution of the system: the carbonyl bands of $\text{Mn}_2(\text{CO})_{10}$ disappear, while new absorptions at 2024, 1886, and 1855 cm^{-1} can be seen to increase progressively (Fig. 3). These results agree with what had already been found by us using the ESR technique, i.e., that a new species with $g = 2.005$ and $A_{\text{Mn}} = 8.7$ mT was formed, Figure 1(c).⁷ If the solvent

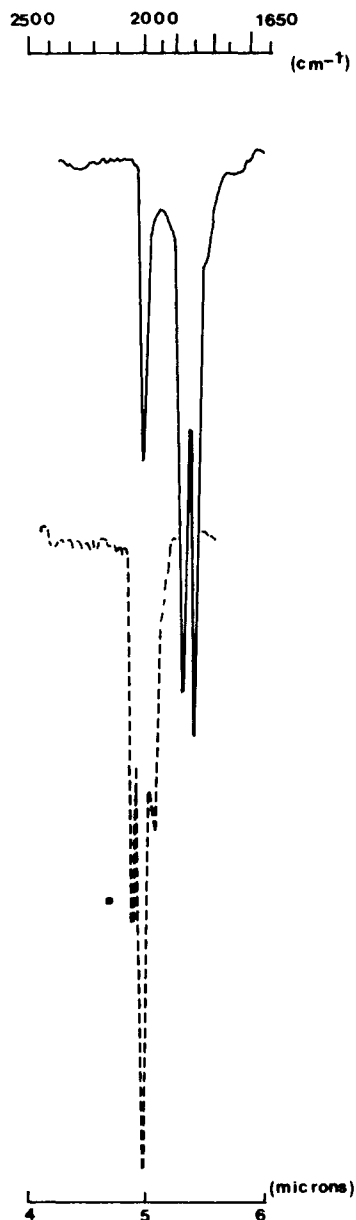


Fig. 3. (—) IR spectrum of an irradiated solution of $\text{Mn}_2\text{CO}_{10}$ in THF- γ -picoline (3:1) at 293 K; (---) IR spectrum of a THF solution of $\text{Mn}_2\text{CO}_{10}$.

is removed by evaporation of the final solution, a powder is obtained whose IR spectrum shows the same carbonyl absorption bands of the solution.

At low temperature the behavior of the system does not differ from the one observed in the absence of ligands. The effect of the temperature has been better assessed with the experiments with *t*-BuNO. It has in fact been found that at room temperature a species containing the nitrogen-donor ligand becomes stabilized, while at low temperature a spectrum equal to that obtained in pure THF has been recorded.⁷

The IR spectra of photolysis carried out in acetonitrile seem to prove complete lack of influence of the nitrogen-donor ligand. Only in the presence of *t*-BuNO did the ESR spectra show evidence of an extremely low concentration of $\text{Mn}(\text{CO})_4(\gamma\text{-pic})$ radical. In chloroform no data for carbonyl absorption bands could be obtained. With ESR, on the contrary, it is still possible to detect a Mn^{2+} species characterized by an octahedral symmetry F (Fig. 4), with a large tetrahedral distortion, having a *D* value of $\sim 0.16 \text{ cm}^{-1}$.¹²

Photolysis of $\text{Mn}_2(\text{CO})_{10}$ in the Presence of Poly(vinylpyridine)

If finely powdered PVP is suspended in the THF solution and the slurry thus formed is irradiated, it is found that, irrespective of the temperature, both ESR, Figure 1(b), and IR spectra, Figure 5, are analogous to those found with γ -picoline at room temperature. Analogously, photolysis tests carried out in acetonitrile in the presence of PVP give results similar to those obtained with γ -picoline.

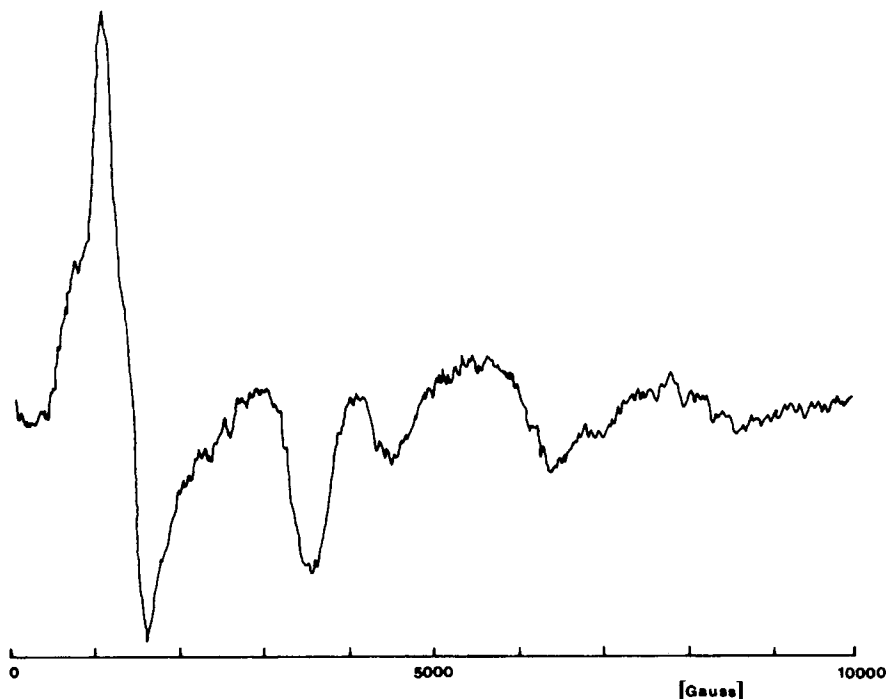


Fig. 4. ESR spectrum of an irradiated solution of $\text{Mn}_2\text{CO}_{10}$ in CHCl_3 - γ -picoline (3:1). Irradiation temperature, 293 K; registration temperature, liquid N_2 .

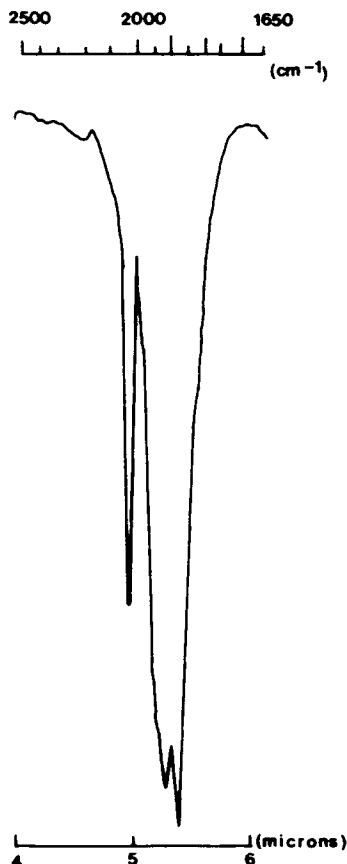


Fig. 5. IR spectrum of PVP isolated from an irradiated solution of $\text{Mn}_2\text{CO}_{10}$ in THF. Irradiation temperature, 293 K.

Conversely, IR spectra of chloroform slurries exhibit the same situation found in the homogeneous phase (absence of carbonyl stretching bands) while ESR spectra show, at both temperatures, a signal lacking hyperfine structure, centered around $g \approx 2$.

DISCUSSION

The results reported in the preceding section indicate that the MnCO_5 disproportionation reaction strongly depends on solvent, temperature, and the presence of nitrogen-donor ligands.

Photolysis in the Absence of Ligands

No evidence of disproportionation reactions has been found by performing the photolysis in THF at room temperature: on the basis of what has been observed by Woiciki and Hughey^{3d} in terms of the recombining rate of $\text{Mn}(\text{CO})_5$ radicals, it seems reasonable to suggest that radical recombination is the only process following the primary photolytic cleavage of the Me-Me bond.

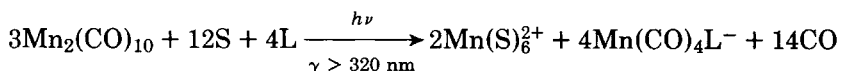
By lowering the temperature, in particular in the region of 240 K, it is possible to activate the disproportioning process; however, IR spectra show only partial evolution of the system in this direction.

In acetonitrile the system behaves in a closely similar way. In chloroform, on the contrary, at both temperatures complete disappearance of $\text{Mn}_2(\text{CO})_{10}$ is observed, accompanied by formation of a paramagnetic manganese species. In consideration of the lack of clear IR evidence and due to the peculiar ESR signal observed in this case, we do not formulate any definite hypothesis as to the type of counterion for Mn^{2+} .

Photolysis in the Presence of Ligands

The situation when a nitrogen ligand is present is significantly different. At room temperature IR spectra obtained in THF with both monomeric and polymeric ligands indicate total disappearance of the carbonyl absorption bands of $\text{Mn}_2(\text{CO})_{10}$ and their replacement with new carbonyl bands. The ESR spectrum also differs from the corresponding spectrum obtained in the absence of a nitrogen-donor ligand. Results obtained by spectroscopic techniques thus appear to confirm the hypothesis we formulated in our previous paper⁷ concerning the partial replacement of ligands on the $\text{Mn}(\text{CO})_5^-$ anion. In fact, the appearance of three IR active bands supports a C_3V symmetry typical of a $\text{Mn}(\text{CO})_4\text{L}^-$ species,^{9,10} while the unsubstituted $\text{Mn}(\text{CO})_5^-$ anion, characterized by a D_{3h} symmetry, has only two IR active bands, as verified experimentally in pure THF.⁹

In conclusion, we may state that at room temperature the disproportionation reaction takes place according to the following scheme:



where S = THF. When the temperature is lowered a more intricate situation is verified. The IR spectrum actually shows superposition of the two spectra corresponding to MnCO_5^- and MnCO_4L^- , respectively. Furthermore, in the course of the first stages of the photoreaction, IR carbonyl absorption bands at about 1950 cm^{-1} have been observed, which had also been previously noted by Brown¹³ during the photolysis of phosphinated complexes $\text{Mn}_2(\text{CO})_9(\text{P}(\text{Et})_3)$ and $\text{Mn}_2(\text{CO})_9(\text{PBu}_3)$ (Fig. 6).

We had already observed that in experiments in which a trap was used, the two radicals MnCO_5^- and MnCO_4L^- could be stabilized at 240 K. It is therefore conceivable that at low temperature also mixed radical recombination occurs with formation of dimeric monosubstituted species. On the other hand, IR spectra of acetonitrile solutions only show evidence of the formation of $\text{Mn}(\text{CO})_5^-$ with exclusion, in the primary reaction stages, of substitute dimeric adducts. Further, experiments with *t*-BuNO indicate a rather low tendency of the system

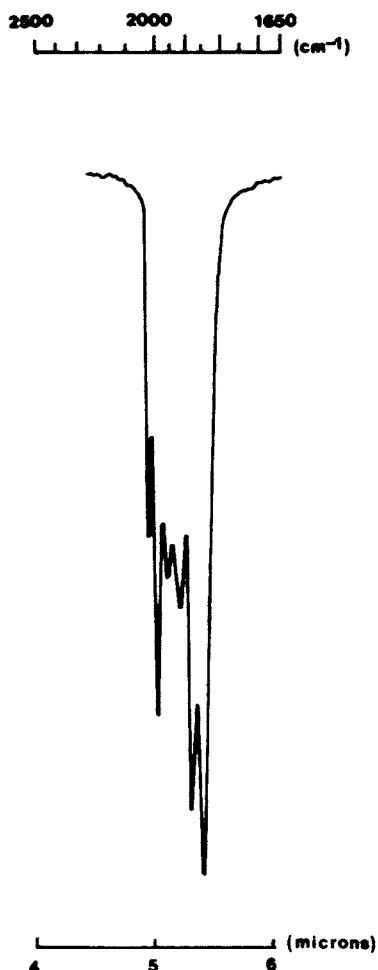


Fig. 6. IR spectrum of a solution of $\text{Mn}_2\text{CO}_{10}$ in THF- γ -picoline (3:1) at the early stages of irradiation at 240 K.

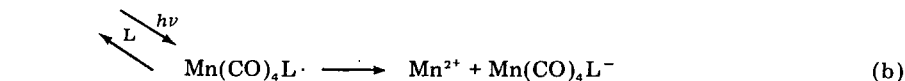
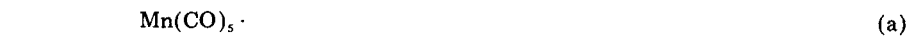
to produce substituted radicals. It is likely that at room temperature recombination of $\text{Mn}(\text{CO})_5$ will prevail over other possible reactions, while at $T = 240$ K the dismutation reaction turns out to be favored analogously to what occurs in the absence of ligands. In chloroform, at both experimental temperatures the ESR spectrum of the photolysis product with γ -picoline has the same magnetic parameters associated with the spectrum reported by Goodgame¹² for $\text{Mn}(\gamma\text{-picoline})_4\text{Cl}_2$. It is obvious that PVP does not allow tetracoordination of pyridine residues around the Mn^{2+} ion.

No correspondence, therefore, can exist between a polymeric ligand and the monomeric model we have adopted. The broad signal at $g \approx 2$ observed in CHCl_3 -PVP should be ascribed, in our opinion, to the same species obtained in CHCl_3 without nitrogen ligands.

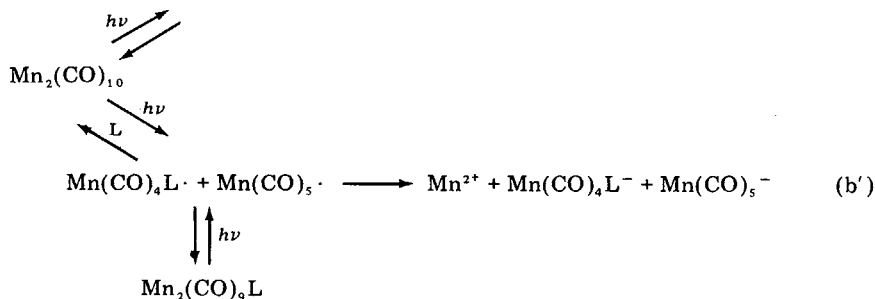
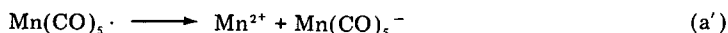
CONCLUSIONS

Our results in THF can be represented by the following scheme:

$T = 293 \text{ K}$:



$T < 240 \text{ K}$:



where $L = \gamma\text{-Pic}$ or PVP.

In acetonitrile the photolytic reaction follows, at both experimentation temperatures, the trend reported in the scheme above in the absence of the ligand L (reaction a, a'), both in the presence and absence of nitrogen ligands.

In chloroform the photoinduced homolytic cleavage of the Mn–Mn bond still leads to the formation of Mn^{2+} ions, although no longer through a disproportionation reaction but eventually through interactions with the solvent.

It can thus be concluded that only in THF is it possible to exploit coordination in order to attach stable manganese species to the polymeric ligand. Such species are being investigated to test their catalytic properties in hydroformylation reactions.

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