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Preliminary communication

Photochemical homolysis of the manganese–manganese bond in decacarbonyldimanganese

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SUMMARY

Photolysis (λ 3500 Å) of $Mn_2(CO)_{10}$ in tetrahydrofuran produces a paramagnetic species which appears to be $Mn(CO)_5^{\bullet}$; it reverts to $Mn_2(CO)_{10}$ on storage and reacts with iodine to give $Mn(CO)_5I$.

Irradiation with ultraviolet light of $Mn_2(CO)_{10}$ in the presence of a ligand L serves as a versatile synthetic route to substituted dimanganese carbonyls, $Mn_2(CO)_{10-x}L_x$[1]. Recently, Gray and coworkers[2] investigated the polarized electronic spectrum of $Mn_2(CO)_{10}$ in nematic solution and assigned the absorption at 29400 cm^{-1} (3400 Å) to an allowed transition between the Mn–Mn σ bond and its corresponding antibonding orbital. Their assignment prompted us to explore the possibility of photochemically inducing another type of a process in $Mn_2(CO)_{10}$, namely scission of the metal–metal bond. Reported herein are our preliminary results.

A degassed tetrahydrofuran (THF) solution of $Mn_2(CO)_{10}$ ($\sim 1 \times 10^{-3}$ *M*) in an evacuated sealed pyrex tube was irradiated for 1–2 h with the 3500-Å lamps in a Rayonet Model RPR-100 Photochemical Reactor. No observable evolution of CO occurred as the solution cleanly changed color from yellow to orange. Upon termination of the irradiation, the orange solution was found to exhibit the following behavior.

(1) When stored at ambient temperatures, it gradually (ca. 1 h) and quantitatively reverted to the yellow solution of $Mn_2(CO)_{10}$.

(2) Addition of it to a solution of iodine in THF under nitrogen gave 30–35% $Mn(CO)_5I$ and 65–70% $Mn_2(CO)_{10}$, based on 90–95% recovery of the manganese. Treatment with CH_3I afforded only $Mn_2(CO)_{10}$. For comparison, $Mn_2(CO)_{10}$ does not react with I_2 at these ambient conditions[3].

(3) Addition of the irradiated solution to 2,2-diphenyl-1-picrylhydrazyl in THF produced rapid orange→violet→green→yellow color changes.

(4) When the irradiation was carried out in an ESR tube, the resulting orange solution showed a six-line signal (I of $^{55}\mathrm{Mn}$-$\frac{5}{2}$) with $\Delta\bar{H}$ 93G and g_{av} 2.00–2.01 (see Fig. 1). This signal faded with time.

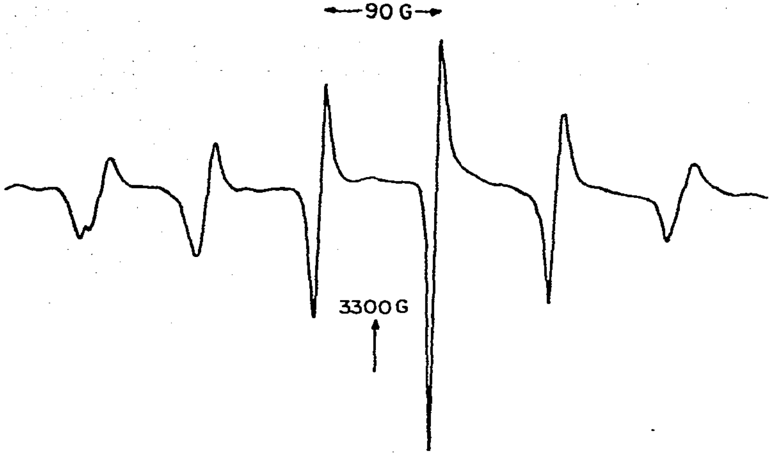

Fig. 1. The ESR spectrum of a freshly irradiated (λ 3500 Å) THF solution of $Mn_2(CO)_{10}$ in an evacuated sealed cell.

(5) Except for the relative intensities, the infrared ν(CO) bands corresponded to those of $Mn_2(CO)_{10}$. However, difficulties were encountered in obtaining a reproducible spectrum because of high sensitivity of the orange solution to oxygen during transfer.

Qualitatively similar results were obtained when the photolysis was performed in a stoppered tube under nitrogen or in an open system under a flow of CO. The use of either 1,2-dimethoxyethane or n-butyl ether in place of THF had no significant effect on the photochemical reaction. However, a freshly irradiated solution of $Mn_2(CO)_{10}$ in cyclohexane contained no reactive species, as indicated by its inertness toward iodine.

The photolysis was also conducted using the Rayonet 3000-Å and 2537-Å lamps. In each case, especially with the 2537-Å light, appreciable decomposition was noted. Addition of the irradiated solutions to iodine afforded 48–66% $Mn_2(CO)_{10}$ and only 1–6% $Mn(CO)_5I$.

By way of contrast, irradiation with the 3500-Å lamps of $Mn_2(CO)_{10}$ in THF under a flow of N_2 or He produced a red solution which did not revert to the original yellow on storage. Its infrared spectrum showed several ν(CO) bands which are not attributable to $Mn_2(CO)_{10}$. Treatment of this solution with $(n\text{-}C_4H_9)_4NI$ led to the isolation in good yield of a carbonyl anion whose infrared spectrum resembles that of $H_2Mn_3(CO)_{12}^-$, synthesized earlier by a similar procedure, with acetone as the solvent[4].

The foregoing observations may be accommodated by the following scheme:

$$\tfrac{1}{2}Mn_2(CO)_{10} \overset{h\nu}{\rightleftharpoons} Mn(CO)_5^{\bullet} \rightleftharpoons Mn(CO)_4^{\bullet} + CO$$

$$Mn(CO)_4^{\bullet} \longrightarrow \text{other carbonyl products}$$

The radical $Mn(CO)_5^{\bullet}$ has been reported to exist in the mass spectrometer above 210° [5], in reactions following the neutron bombardment of $Mn_2(CO)_{10}$ [6], and in thermal reactions involving $Mn_2(CO)_{10}$ [7,8]. Our results suggest that, in a suitable solvent and under conditions preventing escape of CO, $Mn(CO)_5^{\bullet}$ is a reasonably stable species with respect to dimerization or formation of other CO-containing products. However, removal of carbon monoxide (*e.g.* N_2 or He gas flow) leads to its decomposition, possibly through dissociation into reactive $Mn(CO)_4^{\bullet}$ and CO.

Finally, it is noteworthy that irradiation with light having λ 4358 Å of $Mn_2(CO)_{10}$ in acetylacetone or cyclohexanone has been reported to generate $Mn(CO)_4^{\bullet}$ and $Mn(CO)_6^{\bullet}$ [9] Although the results presented herein do not unequivocally eliminate such unsymmetric Mn–Mn bond homolysis in our work, we feel that the formation of $Mn(CO)_5^{\bullet}$ is the simpler explanation which does not require postulation of an energetically unstable $Mn(CO)_6^{\bullet}$. Further support for the symmetric bond scission is furnished by the unreactivity of the irradiated solution toward $P(C_6H_5)_3$ or $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ ($Mn(CO)_4^{\bullet}$ is expected to react) and by the similarity of the results when the photolysis is conducted under a CO flow, static N_2, or vacuum.

Experiments are in progress on oxidation of the paramagnetic manganese carbonyl with 7,7,8,8-tetracyanoquinodimethane (TCNQ) and characterization of the resulting product. Preliminary data on the isolated green solid indicate an approximate composition $[Mn(CO)_3(THF)(TCNQ)]$ and presence of the $TCNQ^-$ radical.

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