Radioactive Manganese Pentacarbonyl Radicals in Neutron-irradiated Manganese Carbonyl Compounds

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IN recent studies of Szilard–Chalmers reactions in manganese carbonyl compounds, there has been evidence[1–3] to suggest the importance of radical reactions, not only in the re-formation of the parent compound, but also in the formation of other compounds. Particularly, ^{56}Mn-labelled MeMn$(CO)_5$ was found[4] in neutron-irradiated methylcyclopentadienylmanganese tricarbonyl, MeCpMn$(CO)_3$, in a reaction which must involve CO groups, Me radicals, and fragments such as Mn$(CO)_x$. Scavenging studies showed[5] that the availability of Me, not of CO, limited the production of MeMn$(CO)_5$. Recent work in this laboratory has shown also[5] that neutron irradiation of benzene solutions of dimanganese decacarbonyl gives rise to phenylmanganese pentacarbonyl, which is probably the unidentified volatile compound reported by Zahn.[3] All of these observations suggest that the Mn$(CO)_5$ radical is a major participant in these reactions, in both the liquid and the solid state.

We have sought more direct proof of the occurrence of this radical in recoil reactions. The experiments involve irradiation of the chosen target compound, dissolution in an appropriate solvent and addition of carriers for the desired compounds, followed by separation of the carriers by column chromatography on silica gel.

We have detected radioactive dimanganese decacarbonyl in neutron-irradiated cpMn$(CO)_3$ and in neutron-irradiated MecpMn$(CO)_3$, suggesting in both cases the combination of two Mn$(CO)_5$ radicals. The experimental results are given in

TABLE 1

Recoil yields in some manganese carbonyl compounds

Target	Compound	Percent yield	
cp$\mathrm{Mn(CO)_3}$	cp$\mathrm{Mn(CO)_3}$	7·5 ± 1·6†	
	$\mathrm{Mn_2(CO)_{10}}$	0·19 ± 0·01	
Mecp$\mathrm{Mn(CO)_3}$	Mecp$\mathrm{Mn(CO)_3}$	7·6 ± 1·1†	
	$\mathrm{Mn_2(CO)_{10}}$	0·1	
	Me$\mathrm{Mn(CO)_5}$	0·1	Ref. 4, 5
$\mathrm{Mn_2(CO)_{10}}$ in benzene solution	$\mathrm{Mn_2(CO)_{10}}$	0·005—0·04	Ref. 3
	Ph$\mathrm{Mn(CO)_5}$	0·1	Ref. 5

† These values seem to be dependent on the irradiation conditions. Values given are for the present series of experiments.

Table 1, where the yield data refer to the percent of the total ^{56}Mn activity.

Further, on dissolving neutron-irradiated $\mathrm{Mn_2(CO)_{10}}$ in pentane solutions of iodine, we have detected ^{56}Mn-labelled I$\mathrm{Mn(CO)_5}$. We feel that there is no reasonable possibility of isotope exchange during the time of our experiments (< 10 min.) nor were we able to detect any sign of a bulk reaction between iodine and $\mathrm{Mn_2(CO)_{10}}$ under these same conditions. The yield of I$\mathrm{Mn(CO)_5}$ observed in this way is about 3—5% and again seems to vary with some subtle aspect of the experimental conditions. Similar experiments done on neutron-irradiated cp$\mathrm{Mn(CO)_3}$ have shown that in this target too I$\mathrm{Mn(CO)_5}$ is produced at the time of dissolution. Thus, we conclude that the $\mathrm{Mn(CO)_5}$ radical was present in the solid matrix until it was released at the dissolving interface, at which time it was scavenged by the iodine. The data are summarized in Table 2.

TABLE 2

Recoil yields from iodine-scavenged targets

Target	Percent Yield of ^{56}Mn as: cp$\mathrm{Mn(CO)_3}$	$\mathrm{Mn_2(CO)_{10}}$	I$\mathrm{Mn(CO)_5}$
cp$\mathrm{Mn(CO)_3}$	7·7 ± 0·6	0·14 ± 0·01	4·2 ± 0·7
$\mathrm{Mn_2(CO)_{10}}$	—	9·8 ± 1·0	4·1 ± 1·0

While it is still premature to draw many conclusions about the mechanisms or even about the reactions involved, it now seems certain that the reaction chain

$$\mathrm{Mn(CO)}_x + \mathrm{CO} \rightarrow \rightarrow \mathrm{Mn(CO)}_5$$

occurs to a measurable extent, and may well lead to all of those products R$\mathrm{Mn(CO)_5}$ which we observe.

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