CHEMICAL REACTIONS IN SOLID MANGANESE CARBONYL COMPOUNDS

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SUMMARY

Radiochemical methods have been used to detect and study the species formed by isolated atoms in matrices of crystalline manganese carbonyl compounds. In this way, reactions are studied which cannot be observed on a macro scale. It is shown that manganese atoms in neutron-irradiated $C_5H_5Mn(CO)_3$ often form $HMn(CO)_5$, while in $CH_3C_5H_4Mn(CO)_3$ they form both $HMn(CO)_5$ and $CH_3Mn(CO)_5$. In $IMn(CO)_5$ they primarily reform the original substance, while in $Mn_2(CO)_{10}$, a considerable proportion of them appear in the form of the $\cdot Mn(CO)_5$ radical. This radical is shown not to exchange with the $Mn_2(CO)_{10}$ matrix molecules, and to decompose above 60°. It is also shown, on a macro scale, that I_2 reacts in solution with $HMn(CO)_5$ to give $IMn(CO)_5$ not, as has been reported, $Mn_2(CO)_{10}$. Various other reactions are discussed.

INTRODUCTION

In the course of a study[1-3] of nuclear recoil (Szilard–Chalmers) reactions in organomanganese compounds, we have had opportunity to observe several interesting reactions of organometal molecules and molecular fragments which are of a nature practicallly inaccessible to ordinary chemical studies.

These reactions are caused by the release of a very large amount of energy immediately ($< 10^{-12}$ sec) following neutron activation of an atom of the compound. The mechanism of the initial reactions is still unknown, but the process can be illustrated in the following way:

A nucleus (in the present case ^{55}Mn) captures a neutron and is thereby transformed into a highly excited state of another isotope (here ^{56}Mn). The excitation energy, which in this case amounts to some 7,000,000 eV, is released as gamma rays of corresponding energy. These gamma rays give a strong impulse of translational energy to the activated atom, which may amount to as much as several hundred eV. This impulse tears the atom loose from its original molecule, and projects it through the crystal lattice until its energy has been dissipated (as heat, molecular excitation and molecular dissociation). The chemistry of this atom once it gets stopped is the subject of this study. It must be noted that the atom remains radioactive long after it has been stopped, and as result it can be observed by its radioactivity (in the present case the radioactive atom is ^{56}Mn, which has a half-life of 2.56 h).

Illustrative of the chemical reactions which can occur in these systems is the observation[3] that when one irradiates $CH_3C_5H_4Mn(CO)_3$, some of the radioactive ^{56}Mn appears in the form of $CH_3Mn(CO)_5$, and more as $HMn(CO)_5$. The question of how the manganese atom acquires two more carbonyls has not yet been resolved. It is known, however, that the CH_3 group comes from the ring substituent rather than from atoms of the ring itself, since the same experiment done on $C_5H_5Mn(CO)_3$ produces no $CH_3Mn(CO)_5$, and only $HMn(CO)_5$.

Generally speaking, the experiment consists of neutron irradiation of an organomanganese compound, followed by dissolution of the crystals in a solution of molecular iodine (to scavenge any radicals) and finally by separation (using non-radioactive carriers) of the various components in which the radioactive atoms are ultimately to be found. Before the dissolution, the radioactive crystals are often subjected to thermal "annealing" which may cause various chemical reactions to occur. It is concluded on the basis of much evidence that the reacting species are radicals and other unstable species which survive only because they are trapped in the crystal lattice.

Because of the extremely small quantities of these substances present (10^8-10^9 radioactive atoms) it is quite difficult to characterize these substances and their reactions well; i.e., ESR and mass spectrometric measurements are far too insensitive. Nonetheless, it is possible to gain an insight into the stability and reactivity of certain species locked in the crystal matrix. Several previously unknown compounds have been discovered in this way, for example $C_5H_5Tc(CO)_3^+$ and $Rh(C_5H_5)_2^5$. On this basis, we discuss previously published[3] results on $Mn_2(CO)_{10}$ and $C_5H_5Mn(CO)_3$ and report new work on neutron-irradiated $IMn(CO)_5$, which show the reactions of some of the fragments formed as result of the nuclear activation.

EXPERIMENTAL

$IMn(CO)_5$ was prepared and purified by the usual method[6]. The purity of the compound was checked by its IR spectrum and its melting point [$115°$ (decompn.)]. Each sample was freshly sublimed in vacuum (10^{-3} mm) within 1 h before the neutron irradiation. Other compounds were either obtained commercially or prepared by standard methods, and purified carefully as has already been described[3].

Neutron irradiations were done in the Antimony–Beryllium neutron source of Atomic Energy of Canada, Ltd., in Ottawa[7] which used about 10 kCi of ^{124}Sb, and consequently gave a gamma dose rate of ~ 2 Mrad $\cdot h^{-1}$. Irradiations were mostly of 15–30 min duration, although we have not noticed any dependence of the results on this duration. Neutron irradiation was done in air and in most cases at a temperature of $-78°$. Thermal annealing of the irradiated samples was done using an electric oven thermostatted to within $\pm 0.5°$, and constant to within $\pm 0.1°$. We had found earlier[3] that the final temperature was not reached for about 2 min, and therefore we have used a 6-min total heating time.

Separation of the components was done by column chromatography after dissolution of the samples in a petroleum-ether solution containing a small amount of iodine as scavenger as well as known small amounts of $Mn_2(CO)_{10}$, $IMn(CO)_5$ and other compounds as carriers. Quantitative determination of chemical recovery was done spectrophotometrically[8]. $HMn(CO)_5$ and $CH_3Mn(CO)_5$ were determined

chromatographically as $IMn(CO)_5$ after reaction with I_2, or directly by GLC. In the latter case chemical recovery was determined gravimetrically. Radioactivity measurements were made using a 3″ by 3″ NaI crystal coupled to a 100-channel pulse height analyser. The 840 keV photopeak of [56]Mn and the 445 keV [128]I photopeak were used, with appropriate corrections being made for mutual interference.

RESULTS AND DISCUSSION

$Mn_2(CO)_{10}$

Results obtained for $Mn_2(CO)_{10}$[3] are shown in Fig. 1. Since considerable radioactive $IMn(CO)_5$ is found, it is quite clear that the iodine scavenger reacts rapidly with some species present in the solid to give $IMn(CO)_5$. This initial species
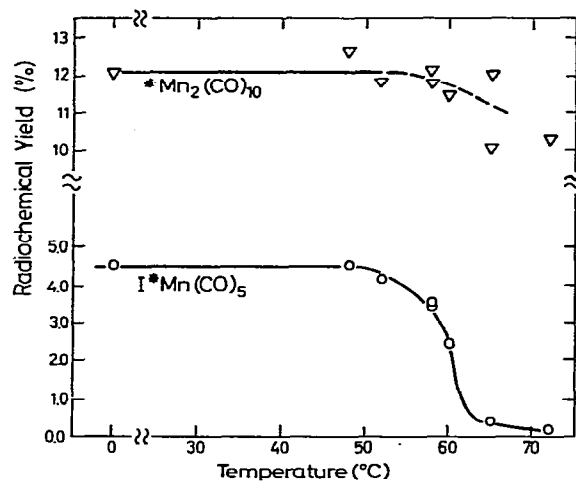

Fig. 1. Radiochemical yield of [56]Mn as *·$Mn(CO)_5$ and *$Mn_2(CO)_{10}$ respectively in neutron-irradiated $Mn_2(CO)_{10}$, following 6 min heating at various temperatures.

is stable in the solid at room temperature for 2 h or more, but decomposes quickly above about 60°. In petroleum ether solution without I_2, this species has a lifetime of 30–40 sec at a temperature of about 20°[3]. It has been concluded[9] that this unstable species must be the ·$Mn(CO)_5$ radical trapped in the solid matrix. This radical, then reacts on dissolution with the iodine scavenger:

$$\tfrac{1}{2}I_2 + \cdot Mn(CO)_5 \rightarrow IMn(CO)_5 \tag{1}$$

The fact that the yield of radioactive $Mn_2(CO)_{10}$ does not increase as the ·$Mn(CO)_5$ decomposes shows that the exchange reaction:

$$* \cdot Mn(CO)_5 + Mn_2(CO)_{10} \rightleftarrows *MnMn(CO)_{10} + Mn(CO)_5 \tag{2}$$
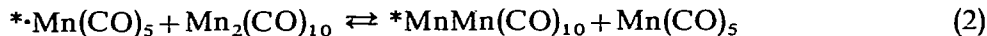
does not occur rapidly in the solid state*.

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* The symbol * indicates that the atom following it is radioactive, and does not imply chemical excitation. When two such atoms are present, as in I_2 and $Mn_2(CO)_{10}$, it is not implied that both are radioactive.

$C_5H_5Mn(CO)_3$

In similar experiments on neutron irradiated $C_5H_5Mn(CO)_3$, radioactive $IMn(CO)_5$ was again found. On heating of the $C_5H_5Mn(CO)_3$, however, the yield of radioactive $I*Mn(CO)_5$ remained constant through heating up to 80°, showing that the unstable $\cdot Mn(CO)_5$ radical was in this case not present but some other, more stable, species was reacting with the iodine. Separate carrier experiments revealed the presence of $H*Mn(CO)_5$ already in the solid[3].

Reaction of I_2 with $HMn(CO)_5$

In non-radioactive, milligram scale studies, it was found that the reaction of I_2 with $HMn(CO)_5$ in pentane solution is rapid, according to the eqn.

$$I_2 + HMn(CO)_5 \rightarrow IMn(CO)_5 (+HI?) \tag{3}$$
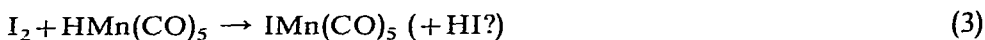
not, as reported in the literature[10], according to

$$I_2 + 2 HMn(CO)_5 \rightarrow 2 HI + Mn_2(CO)_{10} \tag{4}$$
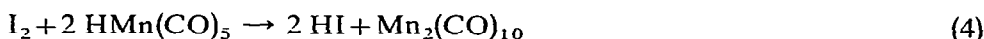
This was shown by allowing the 1/1 (mole ratio) mixture of I_2 and $HMn(CO)_5$ to react together under nitrogen in petroleum ether solution. On analysing the products by column chromatography with air carefully excluded, the only coloured product obtained was $IMn(CO)_5$, and no trace of $Mn_2(CO)_{10}$ was detectable. When a 1/1.5 $[I_2/HMn(CO)_5]$ was used, both $IMn(CO)_5$ and $Mn_2(CO)_{10}$ were found, but Mn_2-$(CO)_{10}$ appeared only after the solution was exposed to air. The reaction thus is according to eqn. (3). Preliminary kinetic studies show that the reaction is first order in I_2. Thus the reaction

$$C_5H_5Mn(CO)_3 + *\cdot Mn(CO)_5 \rightarrow H*Mn(CO)_5 + (?) \tag{5}$$

had occurred at some time only a short time after the nuclear event. $HMn(CO)_5$ evidently does not decompose in the solid $C_5H_5Mn(CO)_3$ matrix.

$IMn(CO)_5$

Results of thermal treatment of neutron-irradiated $IMn(CO)_5$ are shown in Fig. 2. Several things are evident from these data:

(i). The retention of radioiodine in $*IMn(CO)_5$ after 6 min thermal annealing increases with increasing temperature, up to about 80°. Above this temperature, the onset of chemical decomposition causes the data to be badly scattered. The increase in retention is most easily explained as resulting from an exchange reaction:

$$*I + IMn(CO)_5 \rightarrow *IMn(CO)_5 + I \tag{6}$$

We have shown[11] that the reaction

$$*I_2 + IMn(CO)_5 \rightarrow *IMn(CO)_5 + I_2 \tag{7}$$

occurs only slowly in petroleum ether solution. The radioactive iodine involved in reaction (6) must certainly be atomic in form (since the concentration is far too low to allow molecule formation) and is located in a region of the crystal which has been severely stressed as result of the nuclear reaction. Thus, the solid state reaction need not be similar to that in the solution.
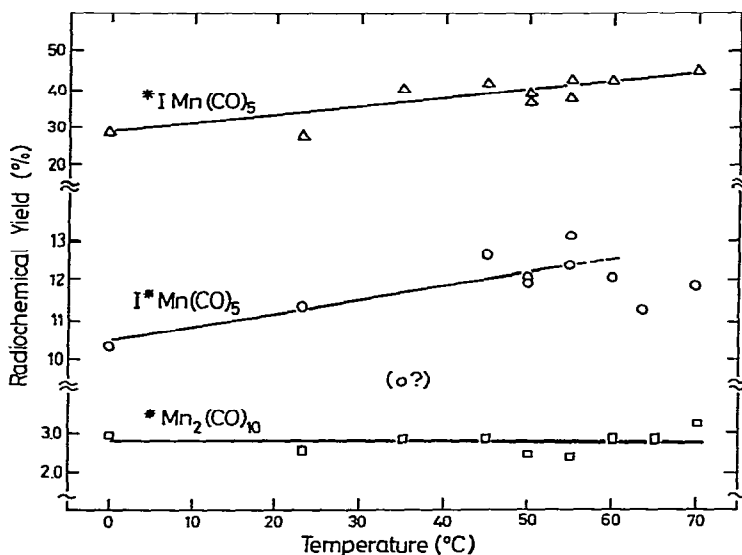
Fig. 2. Radiochemical yields of ^{56}Mn and ^{128}I as *Mn$_2$(CO)$_{10}$, I*Mn(CO)$_5$ and *IMn(CO)$_5$, respectively, in neutron-irradiated IMn(CO)$_5$, following 6 min heating at various temperatures.

(*ii*). The retention of radiomanganese in I*Mn(CO)$_5$ increases slowly with increasing temperature, up to about 60°. Since *·Mn(CO)$_5$ would already be included with I*Mn(CO)$_5$ in our experiment [reaction (1)], the reaction

$$IMn(CO)_5 + *{\cdot}Mn(CO)_5 \rightleftharpoons I^*Mn(CO)_5 + {\cdot}Mn(CO)_5 \tag{8}$$
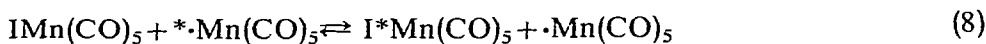
while a plausible reaction, cannot alone account for the data in Fig. 2. Thus, the critical reaction must be a CO transfer, such as

$$*{\cdot}Mn(CO)_4 + IMn(CO)_5 \rightarrow *{\cdot}Mn(CO)_5 + IMn(CO)_4 \tag{9}$$
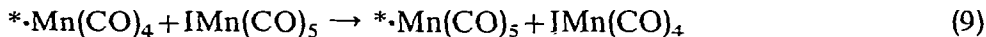
which can then be followed by reaction (8). The observation of lower I*Mn(CO)$_5$ yields at temperatures above about 55° is consistent with the known instability of ·Mn(CO)$_5$, as is shown in Fig. 1, and confirms the participation of this radical in reaction (8).

(*iii*). The yield of *Mn$_2$(CO)$_{10}$ remains approximately constant. This shows that the reaction

$$IMn(CO)_5 + *{\cdot}Mn(CO)_5 \rightarrow *Mn_2(CO)_{10} + {\cdot}I \tag{10}$$
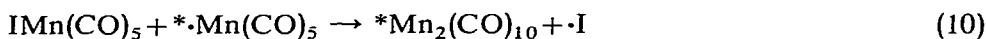
does not compete favourable with reaction (8).

(*iv*). The initial retention of radioiodine in IMn(CO)$_5$ is considerably higher than the corresponding retention of manganese. The origin of this difference can lie either in purely nuclear effects (such as great differences in the Auger vacancy cascades for ^{128}I and ^{56}Mn) or in the fact that atomic iodine is much more likely to be in a position to react than the manganese, which must first assemble five carbonyls and only then form IMn(CO)$_5$, or again in the comparative stability of the MnO bond compared to IO, so that *Mn could be internally scavenged more effectively than *I by oxygen atoms produced *in situ* by the nuclear event. Examples of this last are given by Grossman[12] for various phenylarsenic compounds.

(v). We note that *IMn(CO)$_5$ increases from 29 % to 45 % as the temperature increases while I*Mn(CO)$_5$ increases only from 10.3 % to about 12.3 % and then apparently decreases again [see (ii) above]. The much greater effect of temperature on the reformation of *IMn(CO)$_5$ than of I*Mn(CO)$_5$ is presumably due to the greater ease of reaction of the *I atoms than of *Mn(CO)$_x$ fragments, as was mentioned above.

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