Metal Carbonyl Chemistry Studied with Implanted Ions

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Summary Bombardment of organometallic compounds with radioactive metal ions has been studied with a view to simulating the chemical effects of nuclear transformations; implantation of 4 keV $^{56}Mn^+$ ions into crystalline $Cr(CO)_6$ gives small yields ($<1\%$) of $-Mn(CO)_5$ and $-Mn(CO)_4$.

WE have designed and built an ion accelerator to simulate the chemical processes associated with the production of newly-formed radioactive atoms. Since generation of a high charge on a selected atom in a condensed state would be very difficult or impossible, there is no practicable alternative to implanting radioactive atoms into the solid targets. The accelerator is essentially a 90° sector-type mass spectrometer, with high beam current ($> 1\mu A$) and only moderate resolution (1:100). We report the first results of metal ion bombardment of a molecular organometallic compound. Two other experimental studies[1,2] of metal ion beams on ionic compounds have been reported.

TABLE. *Yields of molecular species from bombardment of* $Cr(CO)_6$ *with* 4 keV $^{56}Mn^+$ *ions.*

Experiment[a]	Yield (%) $-^{56}Mn(CO)_5$	Yield (%) $-^{56}Mn(CO)_4$
No treatment	0·79	0·69
Heated at 74°	0·29	—
Heated at 110°	0·09	0·01
Bombarded with 10 μC of $^{55}Mn^+$	2·0	0·55

[a] This indicates the treatment of the radioactive target following $^{56}Mn^+$ bombardment prior to chemical handling.

$^{56}Mn^+$ beams were used because of the convenient half-life of ^{56}Mn (2·6 h). Manganese is readily volatilized from the metallic state, so that a beam of several μA of ^{55}Mn is easily obtained. The $^{55}Mn^+$ and $^{56}Mn^+$ are well separated at the target, although it is possible some stray current of $^{55}Mn^+$ ($\leqslant 10^{-3}\,\mu A$) may be included in the radioactive beam.

Targets of $Cr(CO)_6$ have been used, both because the CO ligands have been found[3] to be available for certain radiochemical reformation reactions, and because the products expected are few [$-Mn(CO)_5$ and $-Mn(CO)_4$] and easily separable. The chemical reactions expected are as in equation (1).

$$^{56}Mn + Cr(CO)_6 \rightarrow\rightarrow\rightarrow -Mn(CO)_4 \rightarrow -Mn(CO)_5 \qquad (1)$$

$Cr(CO)_6$ is thus sublimed on to a target holder *in situ* at *ca.* 10^{-6} Torr and liquid nitrogen temperature, this is rotated into position and bombarded with a previously aligned $^{56}Mn^+$ beam. After the target is sufficiently radioactive to make subsequent measurements reasonably reliable (20—60 min) the target and its holder are removed and dropped quickly, under a stream of nitrogen, into a $CHCl_3$– light petroleum solution which contains $IMn(CO)_5$ and $[IMn(CO)_4]_2$ as carriers for the $-Mn(CO)_5$ and $-Mn(CO)_4$. (These species have been found to exchange rapidly in solution with the carriers used.) Following chromatographic separation, these carriers are weighed and their ^{56}Mn content is measured by NaI scintillation counting. The radiochemical yield as reported is that fraction of the total radioactive manganese on the target which is found in the specified chemical form.

The Table shows the results of several 'normal' bombardments and of several experiments in which the targets were heated for 20 min at the indicated temperature after the bombardment. This latter treatment allows thermal reactions to be observed and identified.

The full significance of these data is not yet apparent. It is clear, however, that (i) the thermal behaviour of $\cdot Mn(CO)_5$ in a $Cr(CO)_6$ matrix is similar to that of $\cdot Mn(CO)_5$ in $Mn_2(CO)_{10}$,[4] rather than to that of $Cr(CO)_5$ in $Cr(CO)_6$,[3] and (ii) the yields of the two species, $-Mn(CO)_4$ and $-Mn(CO)_5$, are much smaller than one would expect from an extreme hot-zone model of radiochemical reactions. This seems to show that, at least under these conditions and for this compound, the 'hot zone' formed by the kinetic energy of the recoiling nucleus is not the cause of recombination reactions following neutron capture.

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