

Contribution from the Chemistry Department,
Carleton University, Ottawa, Canada K1S 5B6**Radiochemistry of Organomolybdenum Compounds. 2. Formation of Technetium Compounds by β^- Decay in η -Cyclopentadienyltricarbonylmolybdenum**

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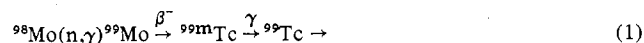
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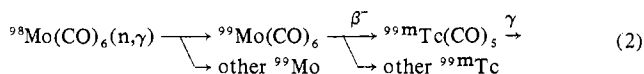
β^- decay of ^{99}Mo in $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ is found to produce $\text{C}_5\text{H}_5^{99\text{m}}\text{Tc}(\text{CO})_3$ in 74.4% of the decays. Comparison with the nuclear recoil energy spectrum and other information leads to the conclusion that this high yield of radioactive product is realized through failure of bond rupture rather than from bond re-formation. The data point to a value of about 10 eV as the minimum kinetic energy required in the solid state for destruction of the molecule by nuclear recoil. A further 2.8% of the $^{99\text{m}}\text{Tc}$ appears as $\cdot\text{Tc}(\text{CO})_5$. The retention of ^{99}Mo as $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ following neutron activation is 13.8%, while 11.5% appears as $^{99}\text{Mo}(\text{CO})_6$. These values are similar to data obtained earlier for $[\text{C}_2\text{H}_2\text{Fe}(\text{CO})_2]_2$ and $(\text{C}_5\text{H}_4)_2\text{Mn}_2(\text{CO})_6$.

The formation of radioactive organometallic compounds by β^- decay of an appropriate radioactive precursor has been known for some time.¹ In particular, the work of Baumgartner and his co-workers has demonstrated the formation of $\text{C}_5\text{H}_5\text{Tc}(\text{CO})_3$ from β^- decay of $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$.² Similarly, $\text{HRh}(\text{C}_5\text{H}_5)_2$ has been formed by β^- decay of $\text{Ru}(\text{C}_5\text{H}_5)_2$.³

In a recent publication,⁴ we demonstrated the formation of the radical $\cdot\text{Tc}(\text{CO})_5$ by using the sequence of nuclear transformations



The β^- decay was used to form $\cdot\text{Tc}(\text{CO})_5$ from $^{99}\text{Mo}(\text{CO})_6$, while the γ emission from $^{99\text{m}}\text{Tc}$ was used to determine quantitatively the relative amounts of $^{99\text{m}}\text{Tc}$ in the various chemical fractions



Although the formation of such compounds by β decay can be explained qualitatively by assuming that previously existing chemical bonds are not broken by the β decay, no attempt has been made to reach a quantitative interpretation of the product yields or any statement of the recoil energies involved.

The nuclear decay scheme⁵ of ^{99}Mo is given in part in Figure 1, in which it can be seen that nearly all of the $^{99\text{m}}\text{Tc}$ atoms are formed following the emission of either a 1.23-Mev β^- or a 0.45-Mev β^- followed by a 0.78-Mev γ ray. These emissions impart a recoil to the resulting nucleus which can readily be calculated for single γ -ray transitions but which depend upon the angular correlation in cases of multiple emission as in γ -ray cascades or β^- -neutrino transitions. We were fortunate in having access to the calculated kinetic energy spectrum⁶ for $^{99\text{m}}\text{Tc}$ atoms recoiling from the β^- decay. It thus seemed to be possible to use this system to develop a deeper insight into the fundamental chemical processes which follow certain nuclear transformations.

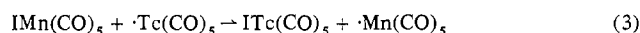
Earlier studies on the radiochemistry of several neutron-irradiated π -ring metal carbonyls have demonstrated the formation of a variety of products. From neutron capture in $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$, for example, radioactive $(\text{C}_6\text{H}_6)_2\text{Cr}$ and $\text{Cr}(\text{CO})_6$ are formed⁷, while in $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$, $\text{HMn}(\text{CO})_5$ and $\text{Mn}_2(\text{CO})_{10}$ are observed⁸ as well as the parent compound in both cases. In all such cases, the metal carbonyls are prominent products. Neutron irradiation of binuclear π -ring metal carbonyls appears to give surprisingly high yields of the radioactive parent compounds, as in $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ ⁹ and $\text{C}_{10}\text{H}_8\text{Mn}(\text{CO})_6$.¹⁰ The apparent preservation of bonds following neutron capture is more surprising in that the nuclear energy to be dissipated is much greater than β^- decay energies

and may well give the product atom a kinetic energy of up to some 500 eV. This is, of course, far in excess of chemical bond energies.

It is appropriate, then, to use the nuclear sequence shown in eq 1 to make a quantitative study of the effects of nuclear transformations in the dimeric $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ both to determine the retention following neutron capture and to study the preservation of bonding following β^- decay. The ultimate objective is to be able to correlate the formation or preservation of bonds with the physical characteristics of the nuclear transformation.

Experimental Section

Reagents. The target compound, $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$, was obtained from Strem Chemicals, Inc., and was purified before use by crystallization from a chloroform-hexane mixture. Other compounds— $\text{Mo}(\text{CO})_6$, $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$, and $\text{IMn}(\text{CO})_5$ —were used as carriers. They were purified by column chromatography, using Davison Grade 923 silica gel, 100–200 mesh, and petroleum ether (bp 35–45 °C) mixed with the chloroform as the eluting agent. It has been shown earlier⁴ that the reaction of the $\cdot\text{Tc}(\text{CO})_5$ radical with pentacarbonylmanganese iodide



is rapid and complete. It was also found that $\text{ITc}(\text{CO})_5$ closely follows $\text{IMn}(\text{CO})_5$ through silica gel chromatography. Likewise, $\text{C}_5\text{H}_5\text{Tc}(\text{CO})_3$ follows $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$. Thus, $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$ and $\text{IMn}(\text{CO})_5$ were used as carriers for $\text{C}_5\text{H}_5(\text{CO})_3$ and $\text{ITc}(\text{CO})_5$, respectively. In both cases, a considerable portion of eluent was collected after the manganese had come off the column, to be sure of getting all of the technetium. The reason for this circuitous procedure is, of course, that the 10^9 – 10^{10} technetium atoms produced are far too few to give a visible band without the added manganese compounds. Moreover, it turns out that the technetium compounds are tightly held by the silica gel unless the manganese analogue is present.

The petroleum ether used for chromatography was redistilled before use (bp 35–45 °C) and was stored over fresh molecular sieves to remove oxygen.

Irradiation and Measurement. Neutron irradiations were done in the Slowpoke Reactor of AECL in Ottawa. The thermal neutron flux was 10^{12} n cm⁻² s⁻¹, the γ flux about 1 Mrad h⁻¹, and the temperature about 35 °C. Irradiation times of 15 min were found to be quite satisfactory for samples containing 150 mg of the target compound.

Radioactivity measurements were made using a 3-in. \times 3-in. NaI scintillation detector and a 512-channel pulse height analyzer. For ^{99}Mo , the 740- and 780-keV γ rays were counted, while for $^{99\text{m}}\text{Tc}$ the 140–143-keV γ -ray pair were counted. Half-life measurements on the 6.0-h technetium confirmed the absence of molybdenum contamination from the purified technetium fractions. Similarly, tungsten contamination of the molybdenum was shown to be negligible.

Procedures and Separations. In a typical experiment, the neutron-irradiated $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ was stored for about 20 h and then divided into several portions, one of which was kept as reference for counting. Each portion to be processed was dissolved in a chloroform

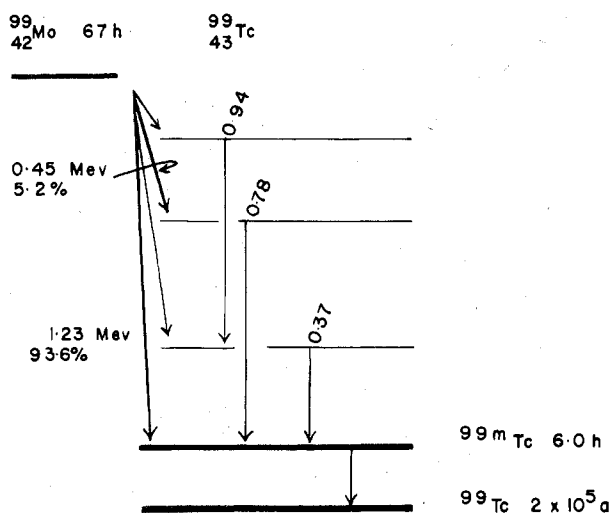


Figure 1. Decay scheme of ^{99}Mo , showing only those transitions which lead to the metastable ^{99m}Tc daughter. Since other transitions are omitted, the transition intensities do not agree with those given in ref 5.

Table I. Experimental Data on Radiochemical Yields of $[\text{C}_5\text{H}_5^{99}\text{Mo}(\text{CO})_3]_2$ (Retention) and $^{99}\text{Mo}(\text{CO})_6$ (Yield) from Neutron-Irradiated $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2]_2^a$

Retention as $[\text{C}_5\text{H}_5^{99}\text{Mo}(\text{CO})_3]_2$, %	Conditions	Yield of $^{99}\text{Mo}(\text{CO})_6$, %
13.2	Room temp	(6.8)
14.2	Room temp	11.4
14.5	Room temp	12.0
12.5	Room temp	
15.4	Room temp	9.3
13.2	Room temp	11.6
13.3	10 min at 58 °C	11.8
13.0	10 min at 86 °C	
14.9	10 min at 93 °C	13.0

^a The average values are $13.8\% \pm 0.4\%$ and $11.5\% \pm 0.5\%$, respectively. Annealing of the $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ was done just prior to chemical processing. The result shown in parentheses is suspect because of very low recovery in the chemical separation.

solution containing weighed amounts of the carriers $\text{Mo}(\text{CO})_6$, $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$, and $\text{IMn}(\text{CO})_5$. After complete dissolution, the CHCl_3 was evaporated off at reduced pressure and the carriers were extracted with a few milliliters of ice-cold petroleum ether. This petroleum ether solution was transferred to a silica gel column made up with petroleum ether. $\text{Mo}(\text{CO})_6$ was eluted with pure petroleum ether, $\text{C}_5\text{H}_5\text{Mn}(\text{Te})(\text{CO})_3$ with 5–10% chloroform, and $\text{I-Mn}(\text{Te})(\text{CO})_5$ with pure chloroform. The $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ residue from the original extraction was dissolved in chloroform, diluted with petroleum ether, and chromatographed on silica gel. The solvents were stripped off each of these effluent solutions; the dried crystals were weighed to determine chemical recoveries and counted.

The purified $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ was weighed, measured, and stored for a further 20 h (cold, in the dark) and then treated with a chloroform solution of $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$ and $\text{IMn}(\text{CO})_5$ carriers for processing as before, to determine the amount of technetium activity in each of the fractions which had grown in from the purified "parent" compound. $\text{Mo}(\text{CO})_6$ carrier was not used in this second stage.

Thermal annealing studies were done on $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ samples heated under nitrogen in an electric oven just before chemical processing. Even though the sample was placed into a beaker of preheated copper shot for quick heating, it was found that it took 2–3 min for the temperature to become established. The data, given in Table I, showed no significant trend as a function of annealing temperature, although a slight increase in retention and yield was observed at the highest temperatures. It therefore seems appropriate to use all of the data in calculating the average values. Uncertainties arising from counting statistics were generally smaller than the overall uncertainties from other sources. Thus, where it was possible, we reported the uncertainties expressed as $\bar{\sigma}$, the standard deviation of the mean values from several independent determinations.

Table II. Retention and Yields of ^{99}Mo and ^{99m}Tc from Neutron Capture and β^- Decay^a

	$[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$	$\text{Mo}(\text{CO})_6$
$^{99}\text{Mo}(n,\gamma)^{99}\text{Mo}$	13.8	11.5
$^{99}\text{Mo} \rightarrow ^{99m}\text{Tc}$		
Purified	$\text{C}_5\text{H}_5\text{Tc}(\text{CO})_3$ 74.4	$\text{Tc}(\text{CO})_5$ 73.5 ^b
Unpurified	20.0	10.6
Calcd	10.3	0.4 → 8.9 ← 8.5
Diff	+9.7	+1.7

^a The data are reported as percent of the total ^{99}Mo (or ^{99m}Tc) activity in the sample before chemical isolation. The "purified" values are those obtained from β^- decay in samples of $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ or $\text{Mo}(\text{CO})_6$ purified after neutron irradiation. "Calcd" values are obtained by applying the "purified" (technetium) yields to the (molybdenum) yields given above for the (n,γ) reaction. "Unpurified" values are those observed for $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ not purified between neutron irradiation and chemical isolation of the technetium products. ^b From ref 4.

Table III. Comparison of Retentions and Yields from Neutron Activation of the Compounds Listed^a

Target	Radioactive product yield, %		
	Dimer	Monomer	Carbonyl
$(\text{CO})_3$ Mn	9.1	0.20	4.4
	16.0	7.4	3.2
	13.8		11.5

^a The "dimer" is in each case the target compound, the "monomers" are respectively $\text{C}_5\text{H}_5^*\text{Mn}(\text{CO})_3$ and $\text{C}_5\text{H}_5^*\text{Fe}(\text{CO})_2$, and the "carbonyls" are $\text{IMn}(\text{CO})_5$, and $\text{Mo}(\text{CO})_6$, where $\text{C}_5\text{H}_5^*\text{Fe}(\text{CO})_2$ and $^*\text{Mn}(\text{CO})_5$ are captured as stable compounds by exchange with nonradioactive carriers, much as is shown in eq 3. For Mn, ref 10; for Fe, ref 9.

Results and Discussion

The results from a variety of experiments are summarized in Table II. Looking first at the 13.8% retention of ^{99}Mo activity in the parent form and the 11.5% yield of ^{99}Mo activity in the carbonyl, $\text{Mo}(\text{CO})_6$, we are able to compare these results with those from the comparable fulvalenehexacarbonyldimanganese, $[(\text{C}_5\text{H}_4)_2\text{Mn}_2(\text{CO})_6]$,¹⁰ and dicyclopentadienyltetracarbonyldiiron.⁶ The values seem to be very similar, as is seen in Table III, except for the yield of $^{99}\text{Mo}(\text{CO})_6$ which is somewhat higher than would have been anticipated from comparison with the manganese and iron results. This higher value is not surprising, however, in view of the more rapid exchange of CO in $\text{Mo}(\text{CO})_6$ than in $\text{Fe}(\text{CO})_5$ or $\text{Mn}_2(\text{CO})_{10}$.¹⁰ It may be that the various $\text{Mo}(\text{CO})_n$ species are more able to accumulate additional carbonyls than are comparable $\text{Mn}(\text{CO})_n$ or $\text{Fe}(\text{CO})_n$ fragments, either because of greater reactivity of the $\text{Mo}(\text{CO})_n$ or because of greater availability of CO in the $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ matrix.

Several experiments were done in which the radioactive sample was annealed for 10 min at temperatures up to 94 °C. While the retention and yield were slightly higher at the highest temperatures used, results at lower temperatures showed no effect, and the increase is not significant. Thus,

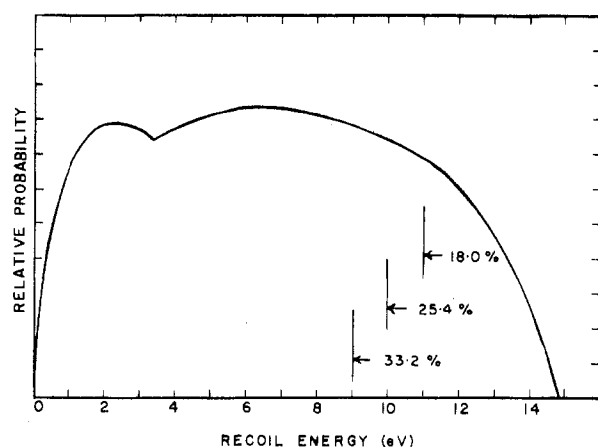


Figure 2. Energy spectrum of ^{99m}Tc atoms recoiling from the two main β^- transitions shown in Figure 1. Numbers on the figure give the percent of the transitions leading to recoil energies in excess of 9.0, 10.0, and 11.0 eV, respectively (from Sundaresan and Watson⁶).

all of these data are included in the mean values given in Table II. The importance of this observation lies in that it shows that all recombination reactions which can occur thermally have already been completed at room temperature, most likely immediately following neutron capture. By contrast, cyclopentadienyldiiron tetracarbonyl shows an increase in $^{59}\text{Fe}(\text{CO})_5$ yield and in the retention of $[\text{C}_5\text{H}_5^{59}\text{Fe}(\text{CO})_2]_2$ on being annealed at temperatures as low as 50–75 °C. Annealing studies have not been done on the corresponding $(\text{C}_5\text{H}_4)_2\text{Mn}_2(\text{CO})_6$.

The yield of $\text{C}_5\text{H}_5\text{Tc}(\text{CO})_3$ from $[\text{C}_5\text{H}_5^{99}\text{Mo}(\text{CO})_3]_2$ which was purified subsequent to the neutron irradiation is found to be quite high—74.4%—and insensitive to the thermal treatment mentioned above. This high value is almost exactly the same as that (73.5%) reported⁴ for the yield of the $\cdot\text{Tc}(\text{CO})_5$ radical from β^- decay of neutron-irradiated $\text{Mo}(\text{CO})_6$. A value of 80–90% is reported¹¹ for the preservation of $\text{Tc}(\text{C}_6\text{H}_6)_2$ formed from β^- decay of $\text{Mo}(\text{C}_6\text{H}_6)_2$. (This value may be somewhat too high, since the experiment involved the use of sublimation at 90 °C to isolate the products—a method shown to give erroneously high results in some cases, because of either annealing or entrainment of foreign species.)

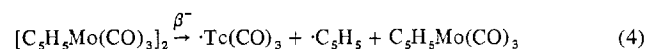
If the nuclear decay were to lead to significant atomic displacement, to be followed by re-formation of the molecule by ligand migration, one would expect the yield of $\text{C}_5\text{H}_5\text{Tc}(\text{CO})_3$ to be lower than that of $\cdot\text{Tc}(\text{CO})_5$, because of the greater mobility of the CO groups. Since this is found not to be the case, the experiments confirm that re-formation of fragmented molecules plays no significant part in the reactions at hand. This conclusion is further confirmed by examining the calculated energy spectrum⁶ for ^{99m}Tc recoiling from β^- decay of ^{99m}Mo . The results are given in Figure 2, from which it is evident that two energy groups occur, corresponding to the two main β^- transitions. The highest energy is calculated to be about 15 eV (and will be slightly lower when appropriate compensation is made for the forbidden character of the β^- transition). The bond energies of this compound are not known, but one can reasonably compare it with $\text{C}_6\text{H}_6\text{Mo}(\text{CO})_3$, for which the bond energies¹² are 1.6 eV for $\text{Mo}-\text{CO}$ and 2.2 eV for $\text{Mo}-\text{C}_6\text{H}_6$ —a total of 7.0. Thus, we can see from the recoil energy spectrum that in many instances there will be insufficient recoil energy to break the bonds and move the technetium atom away from the original molecule. When the recoil energy is below some limiting value, the molecule will be able to absorb the recoil energy as vibrational excitation, which evidently gets dissipated at the surrounding

crystal. Our retention value of 74.4% suggests, by comparison with Figure 2, that a limiting recoil energy of about 10 eV is applicable to both $\text{C}_5\text{H}_5\text{Tc}(\text{CO})_3$ and $\cdot\text{Tc}(\text{CO})_5$ and probably also to $\text{Tc}(\text{C}_6\text{H}_6)_2$.¹¹

One concludes from these results that the dominant phenomenon is retention of structure throughout the β^- decay, rather than any subsequent re-formation reaction. This is possible because of the very small recoil energy imparted to the atom by the combined β^- particle and neutrino. The 0.78-MeV γ ray accompanying about 5% of the decays likewise gives the atom a recoil energy of only about 3.3 eV. In this context, then, the survival of a molecule intact through β^- decay must be a unimolecular process, not dependent on the surrounding matrix as being other than an inert cage able to absorb small amounts of kinetic energy and having an ionization potential equal to that of the target molecule. Any charge effects which might result from the β^- decay¹³ will be rapidly dispersed throughout the molecule and dissipated by intermolecular electron transfer before any atomic motion could be initiated by the Coulomb repulsive forces.

An alternative explanation, which yields approximately correct values for the retention of molecular structure in β^- decay is that involving the “four-fifths” rule of Nefedov and Snell,¹³ who noted that experimental measurements indicate that about four-fifths of the atoms produced by β^- decay in gases develop no charge other than the $1+$ resulting from the increase in atomic number. The assumption is that higher charges will result in Coulomb repulsion sufficient to destroy the molecule. Hence, one-fifth of the molecules will not survive. We do not find this explanation satisfactory for π -bonded solids, where (a) the energy required to move a ligand will be considerably more than the repulsion generated by charges located at reasonable points in the molecule and (b) the charge will most likely be neutralized (or at least diminished) by electron transfer from neighboring molecules long before the atoms can move apart.

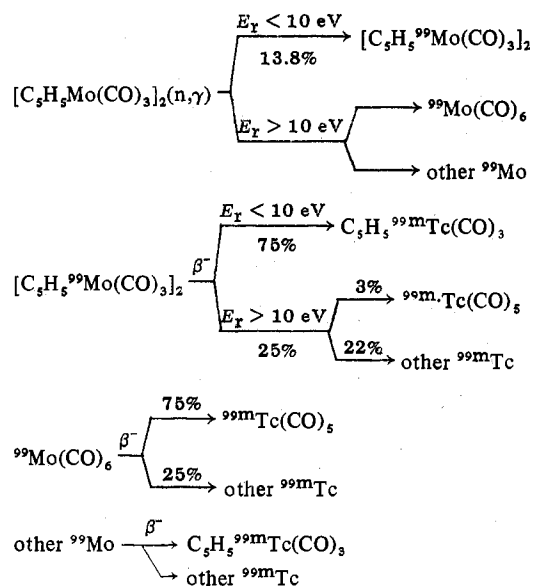
The formation of the $\cdot\text{Tc}(\text{CO})_5$ radical through β^- decay in purified $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ is a rather different matter, however, in that no such precursor molecule had existed— $\text{Mo}(\text{CO})_6$ having been removed in the purification. It is clear that the original molecule has been at least partially dissociated and the cyclopentadiene replaced by two additional carbonyls. This would seem to require substantial displacement of the technetium atom from its original position. The only source of such displacement energy is from the β^- decay, since the recoil energy of ^{99m}Tc from a 0.78-MeV γ ray is only 3.3 eV, while Figure 2 shows that some 25% of the transitions give enough recoil energy to destroy the molecules. The reaction must then be something like



followed by acquisition of two additional carbonyls, perhaps by a process such as that to be described below.

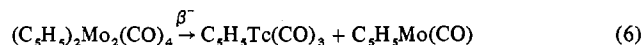
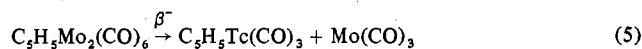
The yields of technetium compounds from the unpurified molybdenum target preparations, as given in Tables I and II, provide further insight into the possible mechanism of re-formation of molecules partially or totally destroyed by nuclear transformations. To assess the magnitude of this effect, we start by calculating the yields of technetium compounds which can be expected from β^- decay of those molecules known to be in an appropriate precursor form at the start of the β^- decay process. This has been done in Table II, where the 13.8% of intact $[\text{C}_5\text{H}_5^{99}\text{Mo}(\text{CO})_3]_2$ molecules were assumed to give $\text{C}_5\text{H}_5\text{Tc}(\text{CO})_3$ in 74.4% of their decays, for an expected yield of 10.3%. For $\cdot\text{Tc}(\text{CO})_5$ there are two sources—the parent compound, which gives $\cdot\text{Tc}(\text{CO})_5$ in 2.8% of the 13.8% remaining $[\text{C}_5\text{H}_5^{99}\text{Mo}(\text{CO})_3]_2$, and $\text{Mo}(\text{CO})_6$, which yields $\cdot\text{Tc}(\text{CO})_5$ in 73.5% of the decays from the 11.5% of ^{99}Mo

Scheme I



atoms found as $\text{Mo}(\text{CO})_6$. The calculated and observed yields are in reasonably good agreement for $\cdot\text{Tc}(\text{CO})_5$, but the yield of $\text{C}_5\text{H}_5\text{Tc}(\text{CO})_3$ is nearly twice as large as is expected from the simplistic calculation above.

This discrepancy could come from one or both of two distinct origins. First, it is possible that the neutron capture reaction may have produced some fragmented molecules, such as $\text{C}_5\text{H}_5^{99}\text{Mo}_2(\text{CO})_6$, $(\text{C}_5\text{H}_5)_2^{99}\text{Mo}_2(\text{CO})_4$, and the like, which would not survive the chemical purification of $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ but which might generate $\text{C}_5\text{H}_5\text{Tc}(\text{CO})_3$ on β^- decay



Such partial molecules would likely recombine with neighboring ligands during thermal treatment and increase the observed retention (as $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$) after annealing. No such effect was found on annealing samples up to 94 °C for 10 min. Furthermore, this same process must also result in fragments which, on β^- decay, should give rise to a substantial increase in the yield of $\cdot\text{Tc}(\text{CO})_5$ —which did not occur.

On the other hand, the decay of an atom by β^- emission will cause considerable local electronic excitation, especially if the

β^- decay is following by a converted γ transition. This can then constitute the activation energy for quasi-chemical reactions which could not occur thermally. This type of local "radiolysis" was first described by Geissler and Willard¹⁴ for the case of certain alkyl halides. The various processes can thus be illustrated as in Scheme I, where E_r is recoil energy. Present evidence, although incomplete, favors the second alternative.

Conclusions

We have shown that the product yields of neutron irradiation of $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ are comparable to those found for other binuclear π -ring metal carbonyls, although there is as yet no explanation for their values. The β^- decay process gives products whose yields are best explained by preservation of the original bonds of the parent compound, where it appears that a recoil energy of more than 10 eV is sufficient to cause effective destruction of the molecule in the solid state. For recoil energies above this threshold energy there are indications that molecules can be formed by epithermal processes initiated by the energy of the β^- decay.

Acknowledgment. We are greatly indebted to Drs. M. K. Sundaresan and P. J. S. Watson, of the Physics Department, Carleton University, for enlightening discussions and for their having calculated the recoil spectrum of $^{99\text{m}}\text{Tc}$, as given in Figure 2. We wish also to acknowledge helpful discussions with Mr. G. M. Jenkins of this laboratory. Financial support was provided by the National Research Council of Canada.

Registry No. $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$, 12091-64-4; $[\text{C}_5\text{H}_5^{99}\text{Mo}(\text{CO})_3]_2$, 60184-31-8; $^{99}\text{Mo}(\text{CO})_6$, 60195-63-3; $\text{C}_5\text{H}_5^{99\text{m}}\text{Tc}(\text{CO})_3$, 60184-30-7; $^{99\text{m}}\text{Tc}(\text{CO})_5$, 41375-71-7; ^{99}Mo , 14119-15-4; $^{99\text{m}}\text{Tc}$, 14133-76-7.

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