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An Electron Spin Resonance Study of Matrix-Isolated Pentacarbonylmanganese(0). Formation from Photolyzed Pentacarbonylhydridomanganese(I)

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Both the infrared and electron spin resonance spectrum of $Mn(CO)_5$ have been misassigned in the earlier literature. Church et al. have finally reported the infrared spectrum of $Mn(CO)_5$, produced by the photolysis of $HMn(CO)_5$ (*J. Am. Chem. Soc.* **1981**, *103*, 7515–7520). We have found corroborating evidence of their conclusions by electron spin resonance spectroscopy. The photolysis of $HMn(CO)_5$ in Ar matrices yields the ESR detectable $Mn(CO)_5$, H·, and HCO. In CO matrices, the photolysis yields only $Mn(CO)_5$ and HCO. The ESR spectrum of $Mn(CO)_5$ is axial with $g_\parallel = 2.00$ and $g_\perp = 2.04$. The manganese hyperfine splitting constants are 65 and −33.5 G for $A_\parallel$ and $A_\perp$, respectively These parameters suggest that the lone electron is localized in a metal-centered orbital consisting mainly of the $3d_{z^2}$ orbital mixed with smaller amounts of the $4p_z$ and 4s orbitals.

Introduction

Church et al. have recently established that photolysis of $HMn(CO)_5$ in a carbon monoxide matrix yields the elusive $Mn(CO)_5$ molecule.[1] Using infrared spectroscopy with ^{13}CO labeling, their results show that $Mn(CO)_5$ has the expected C_{4v} structure, with $\theta = 96 \pm 3°$. The spectrum which they assigned to $Mn(CO)_5$ is considerably at variance to that reported by Huber et al.[2] The latter authors had claimed to have produced $Mn(CO)_5$ by cocondensing manganese metal with CO. Out of this latter work a report appeared of the ESR parameters which were assigned to $Mn(CO)_5$.[3] The work of Howard et al. now confirms that assignment.[4] In view of the doubt cast on the infrared evidence for $Mn(CO)_5$ produced by cocondensation, we consider it of interest to publish the ESR evidence for $Mn(CO)_5$ produced by the photolysis of $HMn(CO)_5$ in matrices.

The search for the ESR spectrum of $Mn(CO)_5$ has resulted in a number of erroneous reports. An early ESR spectrum of sublimed $Mn_2(CO)_{10}$ thought to be due to $Mn(CO)_5$[5] was later shown to be due to $O_2Mn(CO)_5$, no ESR signals being obtained in the absence of oxygen.[6] This was surprising since $Co(CO)_4$ was readily obtained under the same conditions. It was therefore tentatively suggested that $Mn(CO)_5$ was trapped but that its ESR spectrum was broadened by an efficient spin–lattice relaxation process. In the meantime, a species having an isotropic spectrum in the free-spin region with $A(^{55}Mn) = 93$ G, formed by the photolysis of $Mn_2(CO)_{10}$, was also identified as $Mn(CO)_5$.[7] However, this species had properties characteristic of a symmetrical high-spin Mn(II) complex, and this was established conclusively by using S-band ESR spectroscopy.[8]

The concept of rapid relaxation[6] is not supported by the CIDNP studies of Sweany and Halpern,[9] whose data require that $Mn(CO)_5$ have g values close to 2.00. This accords with Burdetts' predictions for $Mn(CO)_5$,[10] and it is clear that $Mn(CO)_5$ should have a well-defined ESR spectrum in the free-spin region that should be readily detectable.

More recently Kidd et al. have observed the ESR spectrum of several derivatives of $Mn(CO)_5$. These complexes have phosphines or phosphites substituted for carbon monoxide to such an extent that the mononuclear species do not dimerize. As such they have reasonably long lifetimes and can be observed at room temperature.[11]

Results and Discussion

The results are summarized in Table I, together with those for some related species. They agree with the spectrum reported by Howard et al. within experimental error although the matrices are vastly different,[4] and they agree with that of Ozin.[3] A typical ESR spectrum is given in Figure 1. The spectrum is axial within experimental error. The $M_I = -^3/_2$ and $-^5/_2$ parallel components are weak and were barely noted above the noise of the base line. Intensity calculations were made analogous to those reported by Neiman and Kivelson which model the gross details of the spectrum, although no actual curve fitting of the derivative spectrum was attempted.[12] In particular, the anomolously large intensity exhibited by the $M_I = ^5/_2$ parallel component is actually derived from a maximum in the intensity for molecules which are neither aligned parallel nor perpendicular to the field. The calculated angle at which the absorption is maximal varies considerably with the input parameters, but for all reasonable estimates, the field position of this maximum overlays the position of $g_\parallel$ to within several gauss. For the parameters listed in Table I, the intensity becomes maximal with $\theta = 17.79°$. Similarly, the intensity of the $M_I = ^3/_2$ perpendicular component, already intense in its own right, is augmented by a maximum in the absorption at $\theta = 81.41°$.

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Table I

	hyperfine splitting					
	$A_\parallel/G$	$A_\perp/G$	a_{iso}/G	$2B/G$	$g_\parallel$	$g_\perp$
$Mn(CO)_5$						
this work	65 ± 4[a]	−33.5 ± 2[a]	−1	+66	2.004 ± 0.010[a]	2.043 ± 0.010[a]
ref 3	±65.8	±32.8				
ref 4	+66 ± 3	−30 ± 3	+2	+64	2.000 ± 0.003	2.038 ± 0.003
$Mn(CO)_3(PBu_3)_2$[10]	±54.1	±35.7	±7[b]		2.040	2.040
$Mn_2(CO)_{10}$[15]	+34.9	−29.2	−7.8	+42.7	1.999	1.998
$Mn(CO)_5Cl^{-\cdot}$[18]	+52.5	−51.3	−16.7	+35.8	2.000	2.001

[a] *g* values and splitting constants are estimated from spectra without regard to second-order effects. [b] Measured value in solution, different from conditions used to measure axial and perpendicular components.

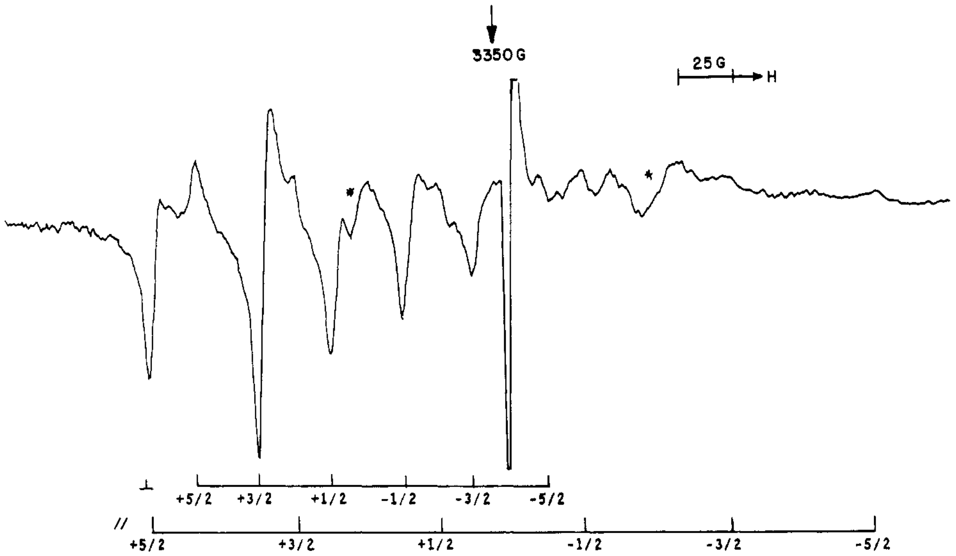

Figure 1. X-band ESR spectrum of $Mn(CO)_5$ in an argon matrix. The spectrum resulted from the photolysis of a 1:1000 mixture of $HMn(CO)_5$ in argon for 40 min. The matrix has been annealed at 20 K, and the hydrogen atom signal has been substantially attenuated. Asterisk marks the absorptions due to HCO.

The situation is analogous to that which was described by Neiman and Kivelson for the $M_I = -^3/_2$ features of a Cu(II) complex. In addition to the features assigned to $Mn(CO)_5$, a central line due to radicals in the quartz vacuum enclosure and weak doublet features for HCO and H are obtained by using argon matrices. When carbon monoxide matrices are used, the intensity for HCO features was greatly increased, and no H atoms were detected. The infrared results[1] show that in argon, the major photochemical act is

$$HMn(CO)_5 \rightarrow HMn(CO)_4 + CO \qquad (1)$$

the reaction

$$HMn(CO)_5 \rightarrow H + Mn(CO)_5 \qquad (2)$$

being minor. Our results show that H· atoms are produced at lower quantum yields in the absence of CO as in the presence of CO. As the progress of photolysis is monitored as a function of time, HCO grows in prior to the observation of H·. Presumably reaction 2 is reversed by a cage effect of unknown efficiency. The H· atom loss processes which are first observed are those which occur in the vicinity of free CO, and the hydrogen atom is trapped by the CO as HCO. With prolonged irradiation, the less probable event of forming simple H· atoms in the matrix is finally observable. This chemistry is analogous to the behavior of $HCo(CO)_4$ in matrices.[13,14] By contrast, the CO loss process of $HCo(CO)_4$ is efficiently reversed, even in the absence of doped quantities of free CO so that little $HCo(CO)_3$ is observed in argon matrices. The CO loss process for both $HCo(CO)_4$ and $HMn(CO)_5$ is effectively reversed in CO matrices and only HCO and the respective metal-centered radicals are observed. Just as is apparent in these spectra, the quantum yield for homolysis increases with the availability of free CO in the matrices, suggesting that there is a cage recombination reaction even for the hydrogen atom loss process.

We consider the identification of the absorbing species in these spectra as $Mn(CO)_5$ is unambiguous in the light of the infrared data on this system and in agreement with previously reported ESR spectra.[3,4] The form of the **g** tensor establishes that the lone electron occupies a nondegenerate orbital which lies on the molecular 4-fold axis. The shift for $g_\perp$ from the free electron value indicates some participation of doubly degenerate orbitals of the *x,y* plane in the HOMO. Conventionally, the HOMO which contains the lone electron would be taken to be mainly the $3d_{z^2}$ orbital of the metal, although the degree of its participation cannot be derived unambiguously from these experiments. Because $A_{iso}(^{55}Mn)$ is unobtainable, there are four alternative ways of analyzing the hyperfine tensor components which are presumed to be principal values. With the electron in an orbital of A_1 symmetry the parallel anisotropic coupling constant (2*B*) should be positive. This is true regardless of the amount of admixture of $4p_z$ in the orbital with the $3d_{z^2}$. For the four permutations of signs of the **A** tensor diagonal elements, only those with $A_\parallel > 0$ give a positive *B*. The $A_\perp$ value may be positive or negative. If it is taken as positive, then the calculated isotropic coupling constant, $a = +44$ G. With a negative $A_\perp$, the value of the isotropic coupling constant is negli-

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gible. We prefer this latter result for two reasons. First, it is quite similar to the reported values for substituted Mn(CO)$_5$.[11] Second, with $a = -1$, the anisotropic coupling constant, $2B$, becomes +66 G, which implies the d orbital contribution to the HOMO is about 60%.[15] The opposite sign for $A_\perp$ would imply only 20% d character in the HOMO.

A small isotropic coupling of ca. zero arises because of a large admixture of the 4s atomic orbital in the half-filled molecular orbital. This adds to the normal value of ca. −90 G which arises from the polarization of the core electrons by a lone electron in the 3d shell. A 4s orbital population of ca. 8% would just cancel out the orbital contribution.[15] It is interesting to note that no ^{55}Mn hyperfine features should be detected in the liquid phase. This will make the solution identification of Mn(CO)$_5$ extremely difficult.

It is interesting to compare these results with those for the (CO)$_5$Mn–Mn(CO)$_5^{-}\cdot$ anion formed by electron attachment to Mn$_2$(CO)$_{10}$.[16] The data, given in Table I, were analyzed in the manner described herein to give 39% each for the two d_{z^2} orbitals and ca. 7% 4s character for each atom. For comparison with the present results, these data should be doubled to give 78% d_{z^2} character and 14% 4s character. While these values are only approximations, nonetheless the trend to greater localization with the d_{z^2} orbitals together with greater 4s character are almost certainly correct.

The increased localization can be understood in two ways. One is that electrons have been shown to be more localized in dimer σ^* radicals than in the corresponding monomers.[15] This was found, for example, for $\cdot$PR$_3$ radicals and R$_3$P–PR$_3^{+}\cdot$ cations[17] and for NO$_2$ and O$_2$N–NO$_2^{+}\cdot$ cations.[18] Probably our present results reflect the same trend. However, we expect to find some tendency for the unpaired electron to favor the space opposite to the axial ligand and to try to avoid the Mn–CO antibonding region. This can best be achieved by admixing 4p$_z$ with the 3d$_{z^2}$ orbital. Since the anisotropic hyperfine coupling for a 4p$_z$ orbital is far less than that for 3d$_{z^2}$, a shift in spin density from 3d$_{z^2}$ into 4p$_z$ would cause a reduction in $2B$, as observed. There is, of course, less if anything to be gained by such admixture for the dimer anion.

The effect of 4s admixture is to increase spin density in the axial lobes of the d_{z^2} orbital and decrease that in the ring lobe. This is favored since it moves the electron away from the antibonding region of the four equatorial ligands. This tendency is apparently slightly reduced for Mn(CO)$_5$ relative to the dimer, and this may accord with the greater tendency for σ^* electrons to become localized.

Comparison with the monohalo anions, Mn(CO)$_5$–halo$^{-}\cdot$ is also of interest.[19] Data for the chloride, also given in Table I, yield 3d$_{z^2}$ and 4s populations of ca. 63% and 6%, respectively. The spin density on manganese is remarkedly close to that for the d_{z^2} orbital of Mn(CO)$_5$, but the 4s character is reduced. The estimated spin density on chlorine was ca. 13%. As with Mn$_2$(CO)$_{10}^{-}\cdot$, there is apparently less to gain for 4p$_z$ admixture in this case. However, a search for ^{13}C hyperfine coupling for the axial CO group was unsuccessful, so either delocalization onto the ligand is small or possibly the ligand was lost on electron addition. It is interesting to note that axial ^{13}C superhyperfine coupling was the only resolved ^{13}C coupling in the analogous Co(CO)$_4$.[20]

Finally, we note that these data for Mn(CO)$_5$ are in agreement with those reported by Ozin.[3] Whatever the difficulty in assigning the infrared spectra, the ESR gives evidence of the existence of Mn(CO)$_5$ in Ozins' matrices. The bands which Church et al.[1] assign to Mn(CO)$_5$ do appear in the spectra reported by Huber et al.[2] The bands are not resolved from a band of Mn$_2$(CO)$_{10}$, however. Thus, we presume, the whole complex of absorptions was assigned to the dimer. Our conclusions are consistent with those of Church et al.[1] The metal–hydrogen bond of HMn(CO)$_5$ does cleave upon photolysis, yielding Mn(CO)$_5$. The process is best observed in the infrared in CO matrices because the competing process of CO loss is suppressed. These complications do not arise when the process is monitored by ESR and, even in argon, homolysis is observed. The ESR shows that Mn(CO)$_5$ also forms in metal–CO cocondensation experiments. Evidence for this occurrence is also provided by the infrared spectrum,[2] but the wrong absorptions were assigned to Mn(CO)$_5$.

Experimental Section

ESR spectra were obtained by using the apparatus which has been described earlier.[13] An impurity in the quartz vacuum shroud provided a sharp signal at $g = 2.005$ for the calibration of the spectra. The matrices were formed either from 1:1000 mixtures of HMn(CO)$_5$ in the dilutent gas or by passing the matrix gas over subliming HMn(CO)$_5$ just prior to deposit. Samples were irradiated with a low-pressure mercury lamp. It was noted from matrix infrared studies that mixtures of HMn(CO)$_5$ in argon which had been stored at room temperature formed some CO. It may have been a product of surface-catalyzed decomposition or due to small amounts of oxygen in the gas sample. Thus, the formation of HCO which observed in photolyzed argon matrices of HMn(CO)$_5$ need not be the result of photogenerated CO reacting with H$\cdot$.

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