Nitrosyltricarbonyl- and Nitrosyldicarbonyl-manganese

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Summary Infrared evidence suggests that photolysis of $Mn(CO)_4NO$ in an argon matrix at 15°K produces CO and metal nitrosyl species which recombine with CO when the temperature is raised from 15°K to 30°K.

RECENT kinetic studies of substitution reactions have suggested that binary transition metal carbonyls principally react by a dissociative (S_N1) process whereas their derivatives readily undergo bimolecular (S_N2) displacement reactions if they contain groups that can delocalise electron density away from the metal, *e.g.* NO, π-C_5H_5, π-C_6H_6.[1] I report the isolation and reactivity of two species produced from $Mn(CO)_4NO$.

Photolysis of a matrix mixture of $Mn(CO)_4NO$ and argon (1 : 200) at 15° K with a filtered medium-pressure Hg arc ($2800 < \lambda < 3600$ Å) produced new i.r. bands in the terminal N–O and C–O stretching frequency regions associated with species (I) (ν_{N-O}: 1733s; ν_{C-O}: 1932s, 1994s, 2072w cm^{-1}) and a band at 2138 cm^{-1} which corresponds to CO. Further photolysis with a different filter $2300 > \lambda > 2800$ Å) produced increases in (I) and CO and new bands associated with species (II) (ν_{N-O}: 1739s; ν_{C-O}: 1967s, 1999s cm^{-1}). The quantity of CO produced was approximately consistent with the loss of one CO per $Mn(CO)_4NO$ in the formation of (I) and further loss in the formation of (II). The i.r. evidence suggests that (I) and (II) are $Mn(CO)_3NO$ and $Mn(CO)_2NO$ respectively with low symmetry structures.†

After raising the temperature of the matrix to 30°K for a few minutes and recooling to 15°K it was found that the isolated species (I) and (II) had reacted with CO to give $Mn(CO)_4NO$. The amount of recombination was comparable with that for $Ni(CO)_3$ and CO at the same temperature.[2] The production of (I) was also reversed by irradiating with $\lambda > 5500$ Å. These observations indicate that, in the absence of radiation which can excite the metal species,

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† A tetrahedral (C_{3v}) structure for $Mn(CO)_3NO$ would have *two* i.r.-active bands in the terminal C–O stretching frequency region whereas *three* are observed.

recombination at temperatures well below 30°K is prevented by an activation energy for the reaction.

In the reactions of $Mn(CO)_4NO$ with a series of nucleophiles it was found[3] that the reaction

$$Mn(CO)_4NO + L \rightarrow Mn(CO)_3(NO)L + CO \qquad (1)$$

followed a two term rate law

$$\text{Rate} = k_1[Mn(CO)_4NO] + k_2[Mn(CO)_4NO][L] \qquad (2)$$

With poor nucleophiles, *e.g.* $AsPh_3$, both terms contributed to the overall rate but with better nucleophiles, *e.g.* PPh_3, the $k_1(S_N1)$ path made almost no contribution and the reaction proceeded by the $k_2(S_N2)$ path. In contrast to this, the monosubstituted derivatives underwent substitution by a dissociative (S_N1) process. The similar rates of the reverse thermal reactions for $Mn(CO)_3NO$, $Mn(CO)_2NO$ and $Ni(CO)_3$ at 30°K suggests that once these species are formed they have low activation energies for the reverse reaction and similar reactivities towards CO and probably other ligands. This means that in the unimolecular process

$$Mn(CO)_4NO \xrightarrow[\text{slow}]{k_1} Mn(CO)_3NO + CO \qquad (3)$$

$$Mn(CO)_3NO + L \rightarrow Mn(CO)_3(NO)L \qquad (4)$$

the second step (4) will be very fast and that CO may compete with L for the $Mn(CO)_3NO$ species.

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