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The exchange of ^{13}CO with manganese pentacarbonyl hydride

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Rate data for the exchange of carbon monoxide with $HMn(CO)_5$ were reported several years ago by Basolo, Brault and Poë[1]. The results, based on observation of ^{14}CO exchange with $HMn(CO)_5$ in dichloroethane as solvent, indicated rapid exchange at −20°. Subsequently the incorporation of ^{13}CO into $HMn(CO)_5$ has been reported[2,3], but no quantitative indications of rate were provided.

Because the reported exchange rate[1] seemed anomalously high in comparison with manganese pentacarbonyl halide exchange[4] and substitution[5] rates, we have reinvestigated carbon monoxide exchange with $HMn(CO)_5$. We find that, contrary to the early report, the exchange is extremely slow.

Manganese pentacarbonyl hydride was synthesized by published procedures[6], and purified by repeated drying and vacuum distillation. The exchange with ^{13}C enriched carbon monoxide was studied in hexane at 40°. The appartus and procedure for carrying out the experiment are described elsewhere[4]. A large molar excess of CO, enriched to the extent of about 20%, was continuously recirculated through a solution containing $1.3 \cdot 10^{-3}$ *M* $HMn(CO)_5$. The entire apparatus was enclosed in a constant temperature compartment within an argon-filled glove box, and protected from exposure to light. Rigorous precautions were taken to exclude light and oxygen at all stages in the preparations and during kinetic runs. Samples withdrawn for IR analysis were loaded into cells in the box and immediately scanned. The incorporation of ^{13}CO was followed by observing the increases in absorbances at 1965 and 1982 cm^{-1} due to axial and radial ^{13}CO incorporation, respectively. The reaction was allowed to proceed for over 300 h to obtain equilibrium absorbance values.

As the exchange proceeds, disubstitution becomes important, and additional, overlapping bands appear, especially near the 1982 cm^{-1} band. We resolved these using a DuPont Model 310 Curve Resolver to obtain estimates of the absorbances due to the axially and radially mono-substituted species at all stages in the reaction.

The ^{13}CO exchange proceeds with a pseudo first-order rate constant at 40° of $6.7 \pm 1.1 \cdot 10^{-6}$ sec^{-1} for radial exchange, and $19 \pm 4.8 \cdot 10^{-6}$ sec^{-1} for axial exchange. The stated uncertainties correspond to 95% confidence limits in the least-squares treatment of the data. Although the exchange is much slower than previously supposed, it is relatively rapid in comparison with the rates expected on the basis of substitution rates for $R_3MMn(CO)_5$ compounds[7]. Furthermore, the radial/axial rate constant ratio is on the order of 0.25–0.5, whereas the same ratio for ^{13}CO exchange with $BrMn(CO)_5$ is 1.35[4].

These comparisons suggest that the exchange proceeds through an acyl intermediate, *i.e.*, via a hydride migration, as suggested by Basolo and Pearson[8].

$$HMn(CO)_5 + {}^{13}CO \longrightarrow HCOMn(CO)_4({}^{13}CO)$$

$$HCOMn(CO)_4({}^{13}CO) \longrightarrow HMn(CO)_4({}^{13}CO) + CO$$

This mechanism should lead to a 1/2 ratio[★] for the radial/axial specific rate constants[4,9], which is not inconsistent with our observations when the possibility of systematic errors is taken into account. The mechanism also implies an overall second order rate law. It is not feasible to effectively têst the rate dependence on CO as we presently perform the experiment. Unfortunately, no rate data for substitution reactions of $HMn(CO)_5$ are available; we have initiated work in this area.

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[★] The total rate of formation of *cis* is twice as great as for *trans*. Since, however, there are four times as many *cis* positions, the specific rate constant for formation of *cis* is 1/2 as great as for *trans*.