Competing Reaction Pathways in the Photochemical Reactions of Manganese Carbonyl Compounds

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Reactive metal carbonyl intermediates exist as coordinatively unsaturated 16-species [1] or as 17-e and 19-e radicals [2]. These intermediates are capable of reacting with main group metal hydrides by any of several pathways. Coordinatively unsaturated 16-e intermediates react via an oxidative addition pathway [3]. 17-e radicals undergo either H-atom atom transfer [4] or oxidative addition [5], whereas, 19-e radicals react via direct H-atom transfer [6].

It has been shown in several studies that irradiation of Mn2(CO)10 leads to two primary photoproducts, Mn2(CO)9 and Mn(CO)5· [7-13]. The photochemical reaction of Mn2(CO)10 and its bis(phosphine) substituted analogs with a main group metal hydride such as HSnBu3 represent a case of competing reaction pathways since both intermediates can potentially exhibit reactivity. To date, the mechanistic details of such reactions remain unclear. In this seminar, results from a continuous photolysis study and a flash photolysis study of the photochemical reaction of Mn2(CO)10 and its bis(phosphine) substituted analogs with HSnBu3 will be presented.

Sunlamp irradiation of a CO-saturated hexane solution of Mn2(CO)10 and HSnBu3 results in formation of HMn(CO)5 and Bu3SnMn(CO)5 in equimolar quantities. The rate of disappearance of Mn2(CO)10 and formation of products exhibit an inverse [CO] dependence. These results are inconsistent with a direct H-atom transfer to Mn(CO)5· as well as oxidative addition of HSnBu3 to Mn(CO)5· via the Brown-Wegman mechanism [5].

When the reaction of Mn2(CO)10 with HSnBu3 is performed under 1 atm Ar, the rate of disappearance of Mn2(CO)10 is much faster than when CO is present, HMn(CO)5 forms in much greater quantities than Bu3SnMn(CO)5, and a third product, identified as HMn(CO)4(SnBu3)2, forms as the other major product. The above observations are consistent with a mechanism involving oxidative addition of HSnBu3 to Mn2(CO)9 as shown in Scheme I.

The wavelength dependence of the quantum yield for product formation is also in accord with a mechanism involving oxidative addition of HSnBu3 to Mn2(CO)9; the quantum yields for product formation and CO loss both increase with decreasing wavelength of radiation, which is opposite to the trend followed for Mn-Mn bond homolysis.

The reactions of HSnBu3 with Mn(CO)4L· (L = CO or PR3) and Mn2(CO)7L2 were studied by flash photolysis. In every case examined, HSnBu3 undergoes oxidative addition with Mn2(CO)7L2. However, H-atom transfer to Mn(CO)4L· does not occur. For L = CO, PMe3, P(i-Bu)3, and P(O-i-Pr)3, the initial product of oxidative addition, Mn2(CO)7L2(H)(SnBu3), is observed. At longer time intervals, this intermediate disappears by reductive elimination of HMn(CO)4L. Mn2(CO)7L2(H)(SnBu3) is not observed when the metal center is crowded as in the cases of L = P(i-Pr)3 and P(C6H11)3 because oxidative addition is slow relative to reductive elimination.
The transient absorbance decay of Mn$_2$(CO)$_7$L$_2$ in the presence of HSnBu$_3$ obeys pseudo-first-order kinetics. Plots of $k_{obs}$ vs. [HSnBu$_3$] are linear for $L = P(i-Bu)$_3$, P(i-Pr)$_3$, and P(C$_6$H$_{11}$)$_3$. However, for $L = PMe$_3$ and P(n-Bu)$_3$, the $k_{obs}$ vs. [HSnBu$_3$] plot is non-linear throughout the entire [HSnBu$_3$] range. A mechanism involving a rate determining equilibrium between unbridged Mn$_2$(CO)$_7$L$_2$ and semi-bridged Mn$_2$(CO)$_7$L$_2$ prior to oxidative addition of HSnBu$_3$ accounts for the experimental observations.

Scheme I

References


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