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Preliminary communication

METAL FORMYL COMPLEXES. THE REACTION OF SODIUM PENTACARBONYLMANGANATE WITH ACETIC [^{13}C]FORMIC ANHYDRIDE

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Summary

The reaction of acetic [^{13}C]formic anhydride with sodium pentacarbonylmanganate proceeds rapidly at 0°C to give ^{13}CO substituted pentacarbonylmanganese hydride as the predominant product. The results are consistent with the formation of a short-lived neutral formyl complex, $(CO)_5Mn—^{13}CHO$.

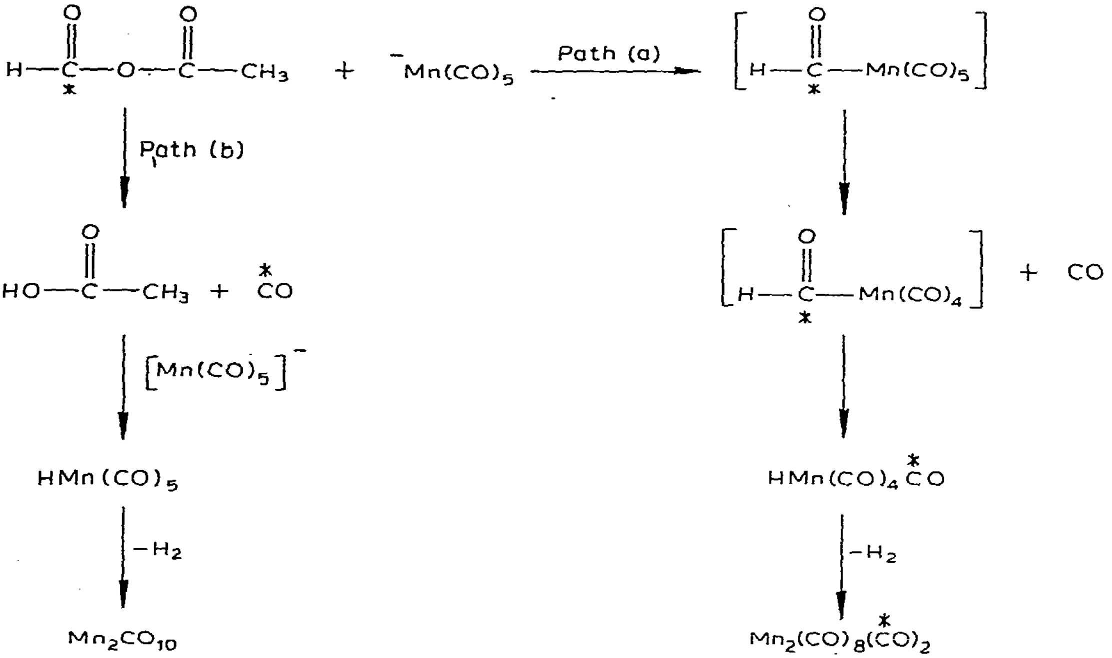
A number of reports have appeared describing both the practical and the theoretical importance of formylmetal complexes [1,2]. For example, Rathke and Feder have implicated the intermediacy of formyl complexes in the homogeneous manganese or cobalt catalyzed conversion of carbon monoxide and hydrogen into methanol [1c]. While a number of anionic derivatives, e.g., $[Mn_2(CO)_9CHO]^-$ and $[RCOMn(CO)_4CHO]^-$, are known [3], attempts to prepare the type of neutral formylmanganese complex that might be expected in that reaction sequence have not been successful.

The preparation of the first kinetically stable formyl complex, $[(CO)_4FeCHO]^-$ was achieved by Collman and Winter [2a] in the reaction of disodium tetracarbonylferrate with acetic formic anhydride. Studies in our laboratories, as well as those reported by Casey and Neumann [2d], have shown that an analogous reaction with lithium or sodium pentacarbonylmanganate does not result in the formation of the anticipated formyl complex, $(CO)_5MnCHO$. Instead, this reaction has been found to give $HMn(CO)_5$ and $Mn_2(CO)_{10}$ in varying yields.

These results are equally consistent with two possible reaction pathways: (a) effective nucleophilic displacement to generate an unstable formyl complex which undergoes decarbonylation to give the corresponding hydride, which can further decompose to the neutral dimer; and/or (b) base catalyzed decomposition of the anhydride to generate acetic acid and carbon monoxide [4], followed by protonation of the pentacarbonylmanganate to generate the hydride and the neutral dimer (see Scheme 1).

If we assume that formyl complex decarbonylation proceeds by loss of a

SCHEME 1



terminal CO, i.e., identical to acetyl complex decarbonylation [5], and that CO exchange with $HMn(CO)_5$ is a slow process [6], then it is possible to distinguish between these two pathways via ^{13}C labeling studies (see Scheme 1). Specifically, by conducting this reaction with acetic [^{13}C]formic anhydride one would expect to find essentially quantitative incorporation of the ^{13}C label in the $HMn(CO)_5$ and $Mn_2(CO)_{10}$ if the reaction proceeds by path (a), and virtually no ^{13}CO incorporation if it proceeds by path (b).

The reaction of sodium pentacarbonylmanganate [7] with 25–50% ^{13}C-enriched acetic formic anhydride [4], prepared by reaction of sodium [^{13}C]-formate with acetyl chloride, proceeds rapidly at 0°C with gas evolution to give pentacarbonylmanganese hydride and decacarbonyldimanganese. While gas evolution ceased after ca. 10 min, reactions were allowed to proceed for an additional 0.5 to 5.5 h period. The gases which were generated were allowed to escape from the reaction system by means of a nitrogen bubbler. On standing, the hydride slowly decomposes with concomitant formation of the neutral dimer. Quantitative mass spectral analysis of this material reveals that it contains the major portion (60–80%) of the ^{13}C utilized in the run. The efficiency of ^{13}C incorporation did not seem to vary as a function of total reaction time, indicating that CO exchange via path (b) was not occurring to a significant degree. These results are consistent with path (a) as the predominant pathway. We should note, however, that Gladysz et al. [8d] have recently demonstrated that a third and unprecedented reaction pathway may be possible, the direct and facile reaction of $HMn(CO)_5$ with neutral formyl complexes. Additional studies will be required before we can establish the importance of this pathway in the title reaction sequence.

Qualitative rate studies have allowed us to place a lower limit on the assumed first-order rate constant for a decomposition of $(CO)_5MnCHO$; $k \geqslant 1.2 \times 10^{-2}$ s^{-1} at 20°C. At 14°C, Gladysz et al. have found that $k = 2 \times 10^{-4}$ s^{-1} for the decomposition of $[Mn_2(CO)_9CHO]^-$ [3a]. The large difference again suggests that anionic formyl complexes are inherently more stable than their neutral analogs [2a,8].

Studies designed to prepare other neutral and anionic formyl complexes are in progress.

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