

Preliminary communication

REACTIONS OF CARBON DIOXIDE WITH METAL CARBONYL ANIONS

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SUMMARY

The reactivity of a series of metal carbonyl anions with CO_2 has been found to parallel their relative nucleophilicities. The highly nucleophilic species, $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2^-$, reacts readily to give the dimer, $(\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2)_2$, and carbonate while $\text{Co}(\text{CO})_4^-$ is unreactive. The reaction of $^{13}\text{CO}_2$ with $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2^-$ results in the formation of the ^{13}CO enriched dimer.

The current interest in the activation of CO_2 via its coordination to transition metal complexes^{1,2,3} and its subsequent conversion (i.e. reduction) into organic materials prompts us to report some of our recent and related studies.

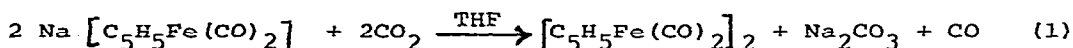
The very modest success of ourselves**and others^{4,5} in converting CO_2 into formate esters in the presence of transition metal catalysts may be attributed in part to the low Lewis basicity of CO_2 and, hence, its general inertness toward coordination to metal complexes. These results have led us to investigate the interaction

**For example, our yield of ethyl formate from a system at 500 psi (1:1 $\text{CO}_2:\text{H}_2$) and 155°C containing a catalytic amount of $\text{C}_2\text{H}_5\text{I}$ in ethanol corresponded to a two molar turnover of $\text{CO}_2(\text{CO})_6(\text{PPh}_3)_2$.

of CO₂ with more "electron rich" species such as the metal carbonyl anions, with a view toward developing catalysts effective in the reduction of CO₂. Indeed, the importance of the basicity of the metal complex in the formation of CO₂ complexes has been alluded to by several authors.^{6,7}

Preliminary experiments have demonstrated that the reactivity of CO₂ with a series of metal carbonyl anions parallels the relative nucleophilicities of these species. For example, Na[C₅H₅Fe(CO)₂]⁻, I, reacts very rapidly in THF with CO₂, while Na[Co(CO)₄]⁻, II, is unreactive under similar conditions for extended periods. It has been reported that I has a nucleophilicity of 70,000,000 on a scale in which II was arbitrarily assigned a value of 1.⁸

The addition of CO₂ to a THF solution of I ($\nu_{\text{CO}} = 1870, 1800, 1770 \text{ cm}^{-1}$) resulted in the rapid uptake of the gas and the immediate conversion (i.e. oxidation) of the anion to the neutral parent dimer, [C₅H₅Fe(CO)₂]₂, III ($\nu_{\text{CO}} = 1990, 1950, 1780 \text{ cm}^{-1}$) accompanied by the formation and liberation of Na₂CO₃. Moreover, the addition of CO₂ to a solution of I stirred with excess sodium amalgam also led to the complete conversion to III. Only when the CO₂ supply was exhausted or removed by purging with N₂ did evidence for the anion reappear in the IR. The amounts of III and Na₂CO₃ recovered from the reaction mixtures suggests that the following scheme (Eqn. 1) must be occurring.



The slow addition of CO₂ to a solution of I has led to the growth of CO stretching bands at 2000 and 1945 cm⁻¹ along with a broad absorption centered around 1400 cm⁻¹ which we suspect may be due to a CO₂ adduct (i.e. [C₅H₅Fe(CO)₂CO₂]⁻). Attempts to isolate this species in the presence of a large cation (i.e. N(C₂H₅)₄⁺ or N(PPh₃)₂⁺) were unsuccessful as were attempts to trap it as a methyl ester by reaction at low temperatures (ca. -68°C) with CH₃I

followed by gradual warming to room temperature. In the latter case, IR spectra revealed that $C_5H_5Fe(CO)_2CH_3$ had formed along with lesser amounts of III. Indeed, I has previously been found to react with CS_2 to give the adduct, $[C_5H_5Fe(CO)_2CS_2]^{-1}$ ^{9,10} which, although not isolated, was reported to react with CH_3I to give the thermally unstable ester, $C_5H_5Fe(CO)_2CS_2CH_3$ ($\nu_{CO} = 2031, 1982 \text{ cm}^{-1}$). ¹⁰

It is very tempting to envision the interaction of the adduct with a second molecule of CO_2 to give $C_5H_5Fe(CO)_2C_2O_4^{-1}$, which by disproportionation might lead to CO_3^{-2} and $C_5H_5Fe(CO)_3^{+1}$. Reaction of the latter with I could then give III and CO. Indeed, Chatt and coworkers ¹¹ have reported that the CO_2 complex, $Mo(CO)_2(PMe_2Ph)_4$, spontaneously converts into the carbonate bridged species, $(PMe_2Ph)_3(CO)Mo(CO_3)_2Mo(CO)(PMe_2Ph)_3$ in solution while Herskovitz ¹² has, in fact, suggested that it is the step-wise reaction of CO_2 with $IrCl(C_8H_{14})(PMe_3)_3$ that leads to a complex containing a chelating ligand (i.e., C_2O_4) derived from two CO_2 molecules. Indeed, we have observed that the reaction of I with labeled $^{13}CO_2$ rapidly (<one minute) gives rise to the dimer, III, greatly enriched with ^{13}CO as evidenced by the increased complexity of the CO stretching spectrum (III, unenriched, 1990 (s), 1950 (s), 1780 (s), cm^{-1} ; III enriched, 1990 (s), 1950 (s), 1920 (m-s), 1780 (m-s), 1750 (m-s) cm^{-1}) as shown in Figure 1. The new bands due to the enriched dimer agree well with those originally weakly observed by Noack ¹³ for the dimer containing naturally occurring ^{13}CO (i.e. 1924 and 1762 cm^{-1} , heptane). This evidence strongly suggests that the CO_2 undergoes coordination followed by reaction at the metal center with the concomitant incorporation of ^{13}CO into the coordination sphere.

The reaction of $Na[C_5H_5NiCO]$, IV, (nucleophilicity=7,500,000) with CO_2 also proceeds rapidly giving carbonate in addition to an unidentified metal carbonyl product other than the neutral

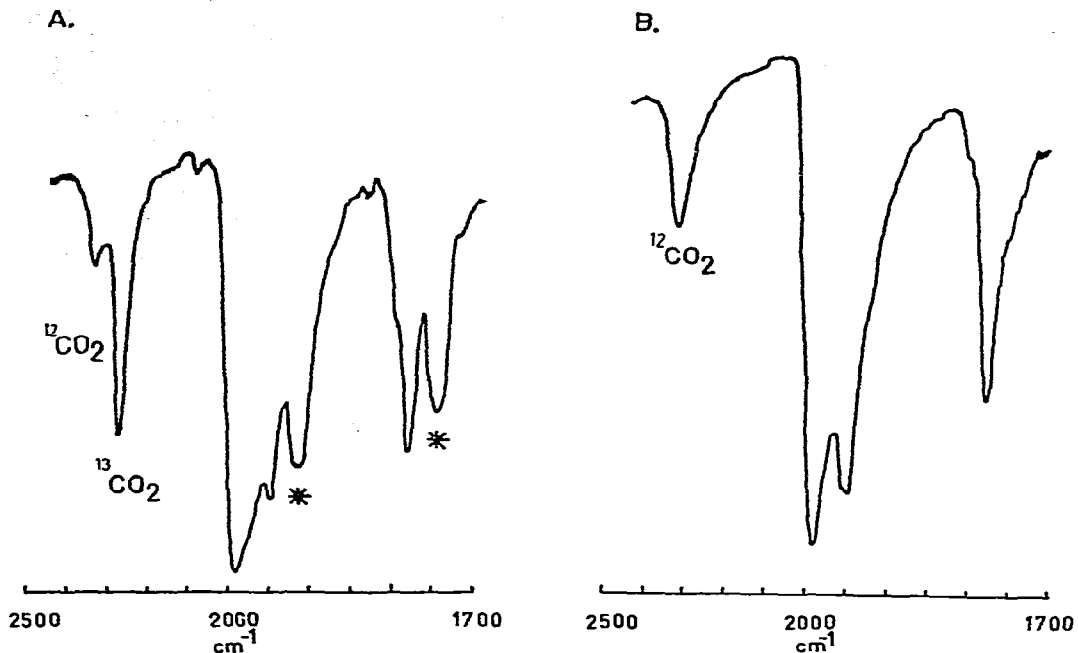


Fig. 1. Comparison of the CO stretching spectra of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ solutions formed from the reaction of $\text{Na}[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]$ with $^{13}\text{CO}_2$ (A) and $^{12}\text{CO}_2$ (B) respectively.

dimer $[\text{C}_5\text{H}_5\text{NiCO}]_2$, V. In addition, $\text{Na}[\text{C}_5\text{H}_5\text{W}(\text{CO})_3]$, VI, (nucleophilicity=500)⁸ has been found to react slowly with CO_2 to give unidentified products while $\text{Na}[\text{Mn}(\text{CO})_5]$, VII, (nucleophilicity=77)⁸ reacts over a period of 24 hours, to give HCO_3^- and an unidentified manganese carbonyl species.

Work is being continued in this area to further characterize and isolate any products and elucidate the mechanisms involved in these reductions.

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