

Conversion of CO₂, H₂, and Alcohols into Formate Esters Using Anionic Iron Carbonyl Hydrides

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While it has long been known that CO₂ could be catalytically reduced with hydrogen into hydrocarbons in the presence of heterogeneous metal catalysts [1], the intensive search for alternative petroleum feedstocks has stimulated much interest in soluble CO₂-transition metal complexes with a view toward their potential role in the activation and homogeneous catalytic reduction of CO₂. Several reviews have recently dealt with this topic [2, 3]. We now wish to report initial studies on the use of anionic metal carbonyl hydrides in the catalytic conversion of CO₂, H₂, and alcohols into alkyl formate esters, a potential intermediate in the reduction of CO₂ into hydrocarbons. Yields, in general, are comparable to those observed using neutral metal phosphine complexes with Lewis acid or base co-catalysts [2, 4, 5].

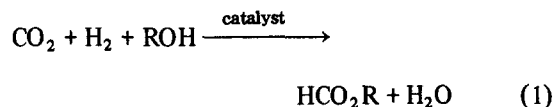
Discussion

A plausible scheme for the homogeneous reduction of CO₂ would very likely involve the coordination of CO₂ followed by its insertion into a metal hydrogen bond to give a metal formate of a metalcarboxylic acid, depending on the polarity of the M–H bond. Indeed, spectral and chemical evidence has been reported in recent years for a variety of CO₂ coordination complexes [2, 3, 6–13] as well as several metal formate complexes [2, 3, 14, 15] and a metalcarboxylic acid [3, 16], formed directly from CO₂ and transition metal hydrides. Although only two X-ray structural studies of CO₂ coordination complexes (*i.e.* Ni(CO₂)(P(C₆H₁₁)₃)₂·0.75C₆H₅CH₃ [6] and IrCl(C₂O₄)(P(CH₃)₃)₃ [9]) have been reported, it is noteworthy that both reports stressed the importance of the basicity of the metal center in its interaction with CO₂. We too, have noted that several highly nucleophilic metal carbonyl anions (*i.e.* C₅H₅Fe(CO)₂[−], C₅H₅NiCO[−], and Re(CO)₅[−]) react readily and irreversibly with CO₂ whereas anions of much lower nucleophilicities (*i.e.* Co(CO)₄[−] and C₅H₅Cr(CO)₃[−]) fail to react under similar conditions [17, 18]. Thus, our search for homogeneous catalysts for the reduction of CO₂ with H₂ has been initially

focused on the use of preformed anionic metal carbonyl hydrides, potentially capable of undergoing both the coordination and insertion of CO₂.

Initial candidates for study have included the HFe(CO)₄[−] and HFe₃(CO)₁₁[−] anions. Both, easily synthesized from Fe(CO)₅ [19, 20], are known to be active in the reduction of nitroaryls [21–23], while a mixture of the two with HFe₂(CO)₈ has been reported to be active in the selective hydrogenation of α, β-unsaturated carbonyl compounds [24].

Although neither [HN(C₂H₅)₃][HFe₃(CO)₁₁] (Ia) nor [N(P(C₆H₅)₃)₂][HFe(CO)₄] (II) appeared to react with CO₂ (*ca.* one atm) in THF as evidenced by little change in the CO stretch region of the IR, it was found that both species, at elevated temperatures and pressures, catalyzed the conversion of CO₂, H₂, and alcohols into alkyl formate esters, detected in the IR spectra of the autoclave gases and quantitatively determined by G.C. analysis on a carbowax 600 column (Tables I and II). In general, [N(P(C₆H₅)₃)₂][HFe₃(CO)₁₁] (Ib) and [HN(C₂H₅)₃][HFe₃(CO)₁₁] (Ia) were found to be more effective than [N(P(C₆H₅)₃)₂][HFe(CO)₄] (II) in Reaction 1 with a maximum conversion (mol formate: mol anion of 5.8:1 observed.



(Table I, Run 9) with Ib in a four-day reaction using CH₃OH at 175 °C and 600 psi (1:1, CO₂:H₂) total pressure. In general, conversions of CO₂ to formate increased with increasing pressures and reaction times as summarized in Tables I and II. Increased temperatures in reactions using I also led to increased yields of formate (Runs 1, 2 and 3, Table I). However, in reactions using II, 150 °C appeared to be the optimum reaction temperature (Runs 1, 2, and 3, Table II). Conversions to methyl formate were also higher than corresponding conversions to ethyl formate. No low molecular weight hydrocarbons, however, have been detected by G.C. analysis of the autoclave gases in these reactions.

No ester formation was observed in the absence of a catalyst although minor amounts of formate were detected in reactions carried out in the absence of H₂ (Table I, Run 15; Table II, Run 11). It is not known at this time whether the formate hydrogen was derived from the hydride ligand or solvent in the latter case. Reactions carried out in the absence of CO₂ gave no formate with Ib (Table I, Run 16) although traces of methyl formate were observed in similar reactions when using II, suggesting that coordinated carbonyl could have been incorporated into the product (Table II, Run 12).

TABLE I. Yields of Alkyl Formates Using Salts of $\text{HFe}_3(\text{CO})_{11}$.

Run	Cation	Alcohol	Temperature (°C)	Reaction		
				Pressure ^a (psi)	Time (hr)	Yield ^b
1	$\text{HN}(\text{C}_2\text{H}_5)_3$	MeOH	125	400	24	1.0
2	$\text{HN}(\text{C}_2\text{H}_5)_3$	MeOH	150	400	24	1.2
3	$\text{HN}(\text{C}_2\text{H}_5)_3$	MeOH	175	400	24	2.2
4	$\text{HN}(\text{C}_2\text{H}_5)_3$	MeOH	150	600	24	2.9
5	$\text{N}(\text{P}(\text{C}_6\text{H}_5)_3)_2$	MeOH	150	400	24	3.5
6	$\text{N}(\text{P}(\text{C}_6\text{H}_5)_3)_2$	MeOH	150	600	24	5.2
7	$\text{HN}(\text{C}_2\text{H}_5)_3$	MeOH	150	400	96	3.8
8	$\text{HN}(\text{C}_2\text{H}_5)_3$	MeOH	150	600	96	4.9
9	$\text{N}(\text{P}(\text{C}_6\text{H}_5)_3)_2$	MeOH	175	600	96	5.8
10	$\text{HN}(\text{C}_2\text{H}_5)_3$	EtOH	150	400	24	1.2
11	$\text{HN}(\text{C}_2\text{H}_5)_3$	EtOH	150	600	24	2.2
12	$\text{HN}(\text{C}_2\text{H}_5)_3$	EtOH	150	400	96	2.0
13	$\text{HN}(\text{C}_2\text{H}_5)_3$	EtOH	150	600	96	2.8
14	$\text{N}(\text{P}(\text{C}_6\text{H}_5)_3)_2$	EtOH	150	400	96	2.1
15	$\text{HN}(\text{C}_2\text{H}_5)_3$	MeOH	150	300 ^c	24	0.4
16	$\text{HN}(\text{C}_2\text{H}_5)_3$	MeOH	150	300 ^d	24	0.0

^aPressure at 25 °C (1:1, $\text{CO}_2:\text{H}_2$). ^bMol of alkyl formate per mol of complex. ^c CO_2 pressure at 25 °C (no H_2 present).^d H_2 pressure at 25 °C (no CO_2 present).TABLE II. Yields of Alkyl Formates Using $[\text{N}(\text{P}(\text{C}_6\text{H}_5)_3)_2][\text{HFe}(\text{CO})_4]$.

Run	Alcohol	Temperature (°C)	Reaction		
			Pressure ^a (psi)	Time (hr)	Yield ^b
1	MeOH	125	400	24	0.5
2	MeOH	150	400	24	1.4
3	MeOH	175	400	24	1.1
4	MeOH	150	600	24	2.0
5	MeOH	150	400	96	1.9
6	MeOH	150	600	96	3.1
7	EtOH	150	400	24	0.9
8	EtOH	150	600	24	1.5
9	EtOH	150	400	96	1.5
10	EtOH	150	600	96	1.6
11	MeOH	150	300 ^c	24	0.4
12	MeOH	150	300 ^d	24	trace

^aPressure at 25 °C (1:1, $\text{CO}_2:\text{H}_2$). ^bMol of alkyl formate per mol of complex. ^c CO_2 pressure at 25 °C (no H_2 present).^d H_2 pressure at 25 °C (no CO_2 present).

Only at reaction temperatures of 125 °C or less, where conversions to formate are quite low, were I or II recovered in their original forms, suggesting that these species are very probably precursors to the active catalysts. Moreover, that carbonate is recovered when using I or II, suggests that a redox process involving the anions and CO_2 is occurring [17] leading to catalyst deactivation. When using I at any

temperature, or II at 125 °C, $\text{Fe}(\text{CO})_5$ is detected in the G.C. of the liquids. There is no G.C. evidence for any iron carbonyl compound when using II at 150° or 175 °C.

We are currently studying the use of a variety of other polynuclear anionic metal carbonyl hydrides [25], hopefully more resistant to oxidation by CO_2 , in the synthesis of alkyl formates or related

esters and their further reduction into alcohols and hydrocarbons.

Experimental

II was prepared by Alper's method [19] and recrystallized from hot ethanol-ethyl acetate solution. Ib was prepared by Case and Whiting's method [20] and recrystallized from methanol-water solution. Ia was prepared by combining a methanol solution of Ib with an equimolar amount of $[N(P(C_6H_5)_3)_2]Cl$, also in methanol solution.

All reactions were carried out in stainless steel autoclaves with 10 ml of solvent and 0.86 mmol of catalyst. The autoclaves were, in general, pressurized with equimolar amounts of CO_2 and H_2 and placed in a shaker in a hot oil bath for the duration of the reaction.

Quantitative studies of the liquids were performed using a Perkin-Elmer 900 Gas Chromatograph equipped with a Carbowax 600 column using a thermal conductivity cell detector. Internal standards were used to calculate yields.

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- 25 For example, $[N(PPh_3)_2][HCr_2(CO)_{10}]$ has given a 9:1 molar turnover in methyl formate formation at 150 °C and 600 psi for 48 hr.