Inorganica Chimica Acta, 31 (1978) L387–L389
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Conversion of CO_2, H_2, and Alcohols into Formate Esters Using Anionic Iron Carbonyl Hydrides

G. O. EVANS and C. J. NEWELL

Department of Chemistry, State University College, Fredonia, New York 14063, U.S.A.

Received August 24, 1978

While it has long been known that CO_2 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 CO_2-transition metal complexes with a view toward their potential role in the activation and homogeneous catalytic reduction of CO_2. 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 CO_2, H_2, and alcohols into alkyl formate esters, a potential intermediate in the reduction of CO_2 into hydrocarbons. Yields, in general, are comparable to those observed using neutral metal phosphine complexes with Lewis acid or base cocatalysts [2, 4, 5].

Discussion

A plausible scheme for the homogeneous reduction of CO_2 would very likely involve the coordination of CO_2 followed by its insertion into a metal hydrogen bond to give a metal formate of a metallocarboxylic 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 CO_2 coordination complexes [2, 3, 6–13] as well as several metal formate complexes [2, 3, 14, 15] and a metallocarboxylic acid [3, 16], formed directly from CO_2 and transition metal hydrides. Although only two X-ray structural studies of CO_2 coordination complexes (*i.e.* $Ni(CO_2)(P(C_6H_{11})_3)_2 \cdot 0.75C_6H_5CH_3$ [6] and $IrCl(C_2O_4)(P(CH_3)_3)_3$ [9]) have been reported, it is noteworthy that both reports stressed the importance of the basicity of the metal center in its interaction with CO_2. We too, have noted that several highly nucleophilic metal carbonyl anions (*i.e.* $C_5H_5Fe(CO)_2^-$, $C_5H_5NiCO^-$, and $Re(CO)_5^-$) react readily and irreversibly with CO_2 whereas anions of much lower nucleophilicities (*i.e.* $Co(CO)_4^-$ and $C_5H_5Cr(CO)_3^-$) fail to react under similar conditions [17, 18]. Thus, our search for homogeneous catalysts for the reduction of CO_2 with H_2 has been intially focused on the use of preformed anionic metal carbonyl hydrides, potentially capable of undergoing both the coordination and insertion of CO_2.

Initial candidates for study have included the $HFe(CO)_4^-$ and $HFe_3(CO)_{11}^-$ 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 $HFe_2(CO)_8$ has been reported to be active in the selective hydrogenation of α, β-unsaturated carbonyl compounds [24].

Although neither $[HN(C_2H_5)_3][HFe_3(CO)_{11}]$ (Ia) nor $[N(P(C_6H_5)_3)_2][HFe(CO)_4]$ (II) appeared to react with CO_2 (*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 CO_2, H_2, 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, $[N(P(C_6H_5)_3)_2][HFe_3(CO)_{11}]$ (Ib) and $[HN(C_2H_5)_3][HFe_3(CO)_{11}]$ (Ia) were found to be more effective than $[N(P(C_6H_5)_3)_2][HFe(CO)_4]$ (II) in Reaction 1 with a maximum conversion (mol formate: mol anion of 5.8:1 observed.

$$CO_2 + H_2 + ROH \xrightarrow{\text{catalyst}} HCO_2R + H_2O \qquad (1)$$

(Table I, Run 9) with Ib in a four-day reaction using CH_3OH at 175 °C and 600 psi (1:1, CO_2H_2) total pressure. In general, conversions of CO_2 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 H_2 (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 CO_2 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 $HFe_3(CO)_{11}^-$.

Run	Cation	Alcohol	Temperature (°C)	Reaction		
				Pressure[a] (psi)	Time (hr)	Yield[b]
1	$HN(C_2H_5)_3$	MeOH	125	400	24	1.0
2	$HN(C_2H_5)_3$	MeOH	150	400	24	1.2
3	$HN(C_2H_5)_3$	MeOH	175	400	24	2.2
4	$HN(C_2H_5)_3$	MeOH	150	600	24	2.9
5	$N(P(C_6H_5)_3)_2$	MeOH	150	400	24	3.5
6	$N(P(C_6H_5)_3)_2$	MeOH	150	600	24	5.2
7	$HN(C_2H_5)_3$	MeOH	150	400	96	3.8
8	$HN(C_2H_5)_3$	MeOH	150	600	96	4.9
9	$N(P(C_6H_5)_3)_2$	MeOH	175	600	96	5.8
10	$HN(C_2H_5)_3$	EtOH	150	400	24	1.2
11	$HN(C_2H_5)_3$	EtOH	150	600	24	2.2
12	$HN(C_2H_5)_3$	EtOH	150	400	96	2.0
13	$HN(C_2H_5)_3$	EtOH	150	600	96	2.8
14	$N(P(C_6H_5)_3)_2$	EtOH	150	400	96	2.1
15	$HN(C_2H_5)_3$	MeOH	150	300[c]	24	0.4
16	$HN(C_2H_5)_3$	MeOH	150	300[d]	24	0.0

[a] Pressure at 25 °C (1:1, CO_2:H_2). [b] Mol 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 $[N(P(C_6H_5)_3)_2][HFe(CO)_4$.

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

[a] Pressure at 25 °C (1:1, CO_2:H_2). [b] Mol 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, $Fe(CO)_5$ 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.

Acknowledgments

The authors would like to thank the donors of the Petroleum Research Fund administered by the American Chemical Society, the Research Corporation and the SUNY Research Foundation for partial support of this work. We also express our appreciation to the U.S. Department of Energy's Pittsburgh Energy Research Center for G.C. Analysis of the autoclave gases.

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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.