Scheme III

$$M(CO)_6 \longrightarrow [M(CO)_5] + CO \quad \xrightarrow{CO + OH^- \rightleftharpoons HCO_2^-}$$
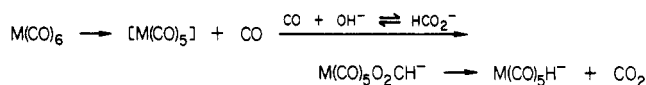
$$M(CO)_5O_2CH^- \longrightarrow M(CO)_5H^- + CO_2$$

as well as comparative rates of R^- addition to the CO ligands in iron and group 6B carbonyls.[63]

These results do not however preclude the presence of $M(CO)_5O_2CH^-$ species during catalysis of the WGSR, for there are several facile routes for their formation once catalysis has ensued which do not require dissociation of CO from $M(CO)_6$.[11] For example, the $[M(CO)_5]$ intermediate afforded upon reductive elimination of hydrogen from $M(CO)_5H_2$ is probably scavenged as effectively by HCO_2^- as by CO, since these pentacoordinate transients are rather indiscriminate in their reactivity toward incoming ligands.[64-66] Of course reaction 2 (i.e., $M-H^- + CO_2 \rightleftharpoons MO_2CH^-$) provides an easy pathway to metalloformate derivatives. In addition, we have some preliminary results in aprotic solvents which suggest that crypt-222 solubilized $KHCO_2$ assists CO loss in $M(CO)_6$ with concomitant formation of $M(CO)_5O_2CH^-$.[67] However, this process is extremely slow relative to hydroxide addition to $M(CO)_6$ and possibly involves an intermediate of the type proposed for the addition of the isoelectronic nucleophile NO_2^- to the carbon center in metal carbonyls.[68]

In summary it is our contention that the premier mechanistic step in the *thermal* catalysis of the WGSR by group 6B metal carbonyls entails activation of carbon monoxide by the transition metal toward nucleophilic attack by hydroxide ions and not by Scheme III as has been suggested by others.[59-61] Indeed activation parameters determined as a function of the metal[59] are inconsistent with such a proposal. On the other hand, photolysis of $M(CO)_6$ in the presence of HCO_2^- can bias the process in favor of a simple formate ion decomposition mechanism as described in Scheme III.[59-61]

(63) Darensbourg, M. Y.; Conder, H. L.; Darensbourg, D. J.; Hasday, C. *J. Am. Chem. Soc.* 1973, *95*, 5919.

(64) Hyde, C. L.; Darensbourg, D. J. *Inorg. Chem.* 1973, *12*, 1286.

(65) Covey, W. D.; Brown, T. L. *Inorg. Chem.* 1973, *12*, 2820.

(66) Dobson, G. R. *Inorg. Chem.* 1980, *19*, 1415.

(67) For example, M(CO)$_6$ (M = Cr, W) in the presence of crypt-222 solubilized KHCO$_2$ in CH$_3$CN at 47 °C exhibits infrared bands assignable to the corresponding M(CO)$_5$O$_2$CH$^-$ species (~5% conversion) after 24 h.

(68) Stevens, R. E.; Yanta, T. J.; Gladfelter, W. L. *J. Am. Chem. Soc.* 1981, *103*, 4981.

Reactions of Formic Acid. 1. The Iridium-Catalyzed Synthesis of Acetic Acid from Methyl Formate[†]

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A very efficient and simple process for "isomerizing" methyl formate to acetic acid utilized a soluble iridium catalyst, promoted by methyl iodide, and was conducted in a carboxylic acid solvent. The acid solvent was found to be necessary and in the simplest case was the product acetic acid. The reaction proceeded in the carboxylic acid by transesterification as a first step, followed by reaction of the formic acid formed in this manner. The rate of formation of acetic acid was a direct function of formic acid, was first order in iridium, and was a positive function of the iodide concentration at lower levels. Water retarded or completely inhibited acetic acid formation and allowed an alternate pathway by which methane and carbon dioxide were the principal products. A mechanism is proposed which involves a unique iridium(III) complex containing hydride, iodide, carbon dioxide, and a methyl group as ligands. Migration of the methyl group to the carbon of the ligated carbon dioxide is the source of acetate. Formaldehyde reacted in this system by first condensing to methyl formate in an iridium-catalyzed Tischenko reaction. This was followed by "isomerization" to acetic acid.

Introduction

Formic acid and methyl formate are simple, versatile products of CO/H$_2$ chemistry. They are unique in that they contain a C–H bond that is aldehyde-like, yet different due to the influence of the C–OH(R) bond. Formic acid is a byproduct of butane oxidation to acetic acid or can be made by the hydrolysis of methyl formate.[1] Methyl

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[†]Dedicated to the memory of the late Rowland Pettit.

(1) (a) Czaikowski, M. P.; Bayne, A. R. *Hydrocarbon Process.* 1980, *59*, 103. (b) Leonard, J. D. U.S. Patent 4 299 981, 1981.

Table I. Thermodynamics of Reactions of Formic Acid
and Methyl Formate

|		
$HCOOCH_3 \rightarrow CH_4 + CO_2$	$\Delta G_{400} = -37.79$	
	$\Delta G_{500} = -40.17$	
$HCOOCH_3 \rightarrow CH_3COOH$	$\Delta G_{400} = -18.53$	
	$\Delta G_{500} = -18.09$	
$HCOOCH_3 \rightarrow CH_3OH + CO$	$\Delta G_{400} = -3.94$	
	$\Delta G_{500} = -7.23$	
$HCOOH \rightarrow CO_2 + H_2$	$\Delta G_{400} = -12.77$	
	$\Delta G_{500} = -15.22$	
$HCOOH \rightarrow CO + H_2O$	$\Delta G_{400} = -6.97$	
	$\Delta G_{500} = -10.38$	

formate is synthesized by base-catalyzed carbonylation of methanol[2] or by dehydrogenation of methanol.[3]

Formic acid and methyl formate may undergo a variety of reactions. Some of these are listed in Table I, together with the thermodynamic force for each. It can be seen that the most favored reaction is the formation of methane and carbon dioxide from methyl formate. Catalysts which promote this reaction must be avoided if other products are desired.

Strong acids decompose formic acid to carbon monoxide and water[5] (eq 1). Heterogeneous catalysts have been

$$HCOOH \xrightarrow{H^+} CO + H_2O \qquad (1)$$
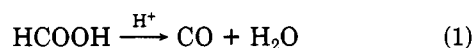
described which cause decomposition to hydrogen and carbon dioxide[6] (eq 2). Similar systems also catalyze the

$$HCOOH \xrightarrow[HI]{[Ir]} H_2 + CO_2 \qquad (2)$$
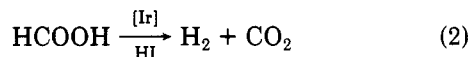
hydrogenation of aldehydes to alcohols[7] and olefins to alkanes[8] (eq 3).

$$HCOOH + [S] \rightarrow SH_2 + CO_2 \qquad (3)$$

S = aldehyde, olefin

A unique reaction which has been mentioned frequently in the patent literature is the "isomerization" of methyl formate to acetic acid. The very early example in the patent literature gave little experimental details but indicated that the active catalysts were metal acetates which decompose with the formation of acetic acid at a temperature between about 200 and 300 °C.[9] A later patent[10] described the use of activated carbon and halogen promoter at 200–400 °C. In one example, a temperature of 350 °C was used with excess carbon monoxide pressure. The yield of acetic acid was about 30%. Since many products are possible from a purely thermodynamic viewpoint (see Table I; also at elevated temperatures, methanol is unstable relative to carbon monoxide and hydrogen[4]),

it is not clear how much, if any, influence of catalyst selectivity has been achieved.

Other systems which have been examined include rhenium halides and methyl iodide,[11] mercury (II) iodide, and excess iodide in amide solvents under 300 atm of carbon monoxide[12] and certain group 8 metals. A comprehensive survey of a cobalt iodide system was that made by Isogai.[12] With a solution of methyl formate in N-methylpyrolidone or in acetophenone, at temperature of 220–230 °C and pressures of 300–400 atm (carbon monoxide and reactants), 90–95% yields of acetic acid were obtained. Antoniades[13] showed that with rhodium, milder temperatures (170–200 °C) and lower pressures (200–500 psi preferred) gave good results.

A mechanistic study of the rhodium–iodide–carbon monoxide catalyzed reaction has been reported by Bryant and co-workers.[14] From the results obtained with ^{14}C-labeled methyl iodide, ^{14}C-labeled carbon monoxide and H[14]COOCH3-labeled methyl formate, each in separate and successive experiments, these workers concluded that the transformation proceeded through decarbonylation to methanol and carbon monoxide, followed by carbonylation of the methanol to acetic acid (eq 4). In particular, the

$$HCOOCH_3 \rightarrow [CH_3OH + CO] \xrightarrow[CH_3I]{[Rh]} CH_3COOH \qquad (4)$$
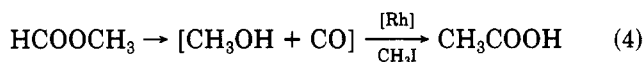
[14]CO-labeled experiment produced maximum CH3[14]COOH incorporation at the early stages, which indicated subsequent dilution with extruded carbon monoxide.

In our studies of homogeneous catalyzed reactions of methyl formate, it was found that soluble iridium compounds, in conjunction with an organic iodide and without carbon monoxide, efficiently catalyze the transformation of methyl formate to acetic acid, but only in the presence of a carboxylic acid. The acid may be, but is not necessarily, the product acetic acid. The reaction occurs in the temperature range 160–210 °C and is highly selective under anhydrous conditions, only autogeneous pressures are necessary. Evidence indicates that the reaction pathway involves formate ligand and probably a coordinated carbon dioxide.

Experimental Section

The reactions were conducted in an Autoclave Engineers 1-L Hastelloy-C autoclave which was fitted with an internal, magnetically driven agitator. Provisions were made by tubing through the head of the autoclave, with appropriate valving, for addition of other reactants if needed, and for removal of samples during the course of the reaction. When samples were taken, usually after 0.5, 1, and 2 h, an equal volume of material (10–15 g) was first removed to flush out liquid trapped in the lines. The reactor was also fitted with an exit line at the bottom to facilitate removal of liquid contents without disassembly of the reactor. However, the reactor was opened periodically to inspect the walls for adventitious solids deposition. A glass liner was used occasionally, but no difference could be detected, and it made the operation more difficult since the reactor needed to be opened following each reaction. Also, solvent and reactant distilled out of the liner in an uncontrolled manner.

The simplest solvent system employed acetic acid. The analyses were simplified from the standpoint of fewest number of peaks, but the product was the difference between two large numbers and thus not accurate. Most experiments utilized propionic acid as solvent. This simplified product analysis but resulted in a large number of intermediate peaks due to transesterification reactions.

(2) Aguilo, A.; Horlenko, T. *Hydrocarbon Process.* **1980**, *59*, 120.
(3) Yoneoka, M. U.S. Patent 4 319 037, 1982.
(4) Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. "The Chemical Thermodynamics of Organic Compounds"; Wiley: New York, 1969.
(5) (a) Haaf, W. *Brennst.-Chem.* **1964**, *45*, 209. (b) Haaf, W. *Chem. Ber.* **1966**, *99*, 1149.
(6) (a) Coffey, R. S. *Chem. Commun.* **1967**, 923. (b) Yurtchenko, E. N.; Anikeenko, N. P. *React. Kinet. Catal. Lett.* **1975**, *2*, 65. (c) Yurchenko, E. N. *Kinet. Katal* **1973**, *14*, 515. (d) Forster, D.; Beck, G. R. *J. Chem. Soc. D* **1971**, 1072.
(7) Coffey, R. S. *Chem. Commun.* **1967**, 923.
(8) (a) Vol'pin, M. E.; Kukolov, V. P.; Chernyshev, V. O.; Kolomnikov, I. S. *Tetrahedron Lett.* **1971**, *46*, 4435. (b) Kolomnikov, I. S.; Kukolov, V. P.; Chernyshev, V. O.; Vol'pin, M. E. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1972**, 693.
(9) Dreyfus, H. U.S. Patent 1 697 109, 1929.
(10) Wakamatsu, H.; Sato, J.; Hamaoka, T. U.S. Patent 3 798 267, 1974.

(11) Japan Kokai 76/65,703, 1976.
(12) Isogai, N. U.S. Patent 3 839 428, 1974. Reissue 29 981, 1979.
(13) Antoniades, E. P. U.S. Patent 4 194 056, 1980.
(14) Bryant, F. J.; Johnson, W. R.; Singleton, T. C. *Am. Chem. Soc., Prepr., Div. Petroleum Chem.* **1973**, *181*, 193.

Table II. Isomerization of Methyl Formate Solvent Effect

expt no.	reactants (g)	catalyst (g)	temp, °C	solvent (g)	t, h	CH$_3$COOH produced, g
II-1a	HCOOCH$_3$ (350)	[Ir(COD)Cl]$_2$ (0.5) CH$_3$I (11.4)	190	none	2	no reaction^a
II-1b				acetic acid (250)	2	41.8, 148 g of CH$_3$COOCH$_3$
II-2	HCOOCH$_3$ (100)	[Ir(COD)Cl]$_2$ (0.5) CH$_3$I (18.2)	190	acetophenone (200)	4	0, 2.0 g of CH$_3$COOCH$_3$
II-3	HCOOCH$_3$ (100)	[Ir(COD)Cl]$_2$ (0.5) CH$_3$I (18.2)	210	propionic acid (222) toluene (170)	4	71.2, 6.1 g of CH$_3$COOCH$_3$
II-4	HCOOCH$_3$ (100)	[Ir(COD)Cl]$_2$ (0.5) CH$_3$I (18.2)	210	propionic acid (148) toluene (250)	4	44.1, 8.3 g of CH$_3$COOCH$_3$
II-5	HCOOCH$_3$ (100)	[Ir(COD)Cl]$_2$ (0.5) CH$_3$I (18.2)	210	propionic acid (74) toluene (320)	4	11.9,^{b} 5.5 g of CH$_3$COOCH$_3$
II-6	HCOOCH$_3$ (300)	[Ir(COD)Cl]$_2$ (0.5) CH$_3$I (22.7)	180	propionic acid (25)	5	0, 3.7 g of CH$_3$COOCH$_3$
II-7	HCOOCH$_3$ (100)	[Ir(COD)Cl]$_2$ (0.5) CH$_3$I (34.1)	190	propionic acid (250)	5	69.8, 7.1 g of CH$_3$COOCH$_3$
II-8	HCOOCH$_3$ (100)	[Ir(COD)Cl]$_2$ (0.5) CH$_3$I (22.7)	180	propionic acid (300) formic acid (72)	4	75.8
II-9	CH$_3$CH$_2$COOCH$_3$ (88) HCOOH (50)	[Ir(COD)Cl]$_2$ (0.5) CH$_3$I (22.7)	200	propionic acid (250)	5	58.4 (97% of theory)
II-10	CH$_3$CH$_2$COOCH$_3$ (74) HCOOH (60)	[Ir(COD)Cl]$_6$ (0.5) CH$_3$I (15.9)	200	acetophenone (250)	4	50.5 (100% of theory)
II-11	CH$_3$CH$_2$COOCH$_3$ (88) HCOOH (96)	[Ir(COD)Cl]$_2$ (0.5) CH$_3$I (22.7)	180	propionic acid (400)	4	45.8
II-12	CH$_3$CH$_2$COOCH$_3$ (88) HCOOH (96)	[Ir(COD)Cl$_2$] (0.5) CH$_3$I (22.7)	180	propionic acid (300)	4	52.7
II-13	CH$_3$CH$_2$COOCH$_3$ (88) HCOOH (96)	[Ir(COD)Cl$_2$] (0.5) CH$_3$I (22.7)	180	propionic acid (200)	4	51.9

^{a} In part b, 250 g of acetic acid was added to the cooled product from part a, then the heating was continued for another 2 h. ^{b} The product contained unreacted methyl formate, methyl propionate, and a purple solid. The purple solid analyzed IrI$_3$.

The products were analyzed by VPC with the use of a Hewlett-Packard 5840A instrument and the thermal conductivity detector. In a few early experiments the column used was a 6 ft × $^1/_8$ in. Chromosorb 101 but most were conducted with a 6 or 10 ft Poropak T, dimethyl formamide as internal standard, programmed from 170 to 190 °C after 15 min at 170 °C. The retention times varied with the age of the column. Typical times (min) on the 10-ft column were as follows: H$_2$O, 2.79; HCOOCH$_3$, 3.70; CH$_3$I, 5.04; CH$_3$COOH, 6.65; CH$_3$CH$_2$COOCH$_3$, 10.60; HCOOH, 16.24; CH$_3$COOH, 19.76; CH$_3$CH$_2$COOH, 24.82; HCO-N(CH$_3$)$_2$, 30.69.

For confirmation of compound identification during early stages of reaction, ^{1}H NMR spectra were obtained on a Varian EM360L spectrometer. The protons in HCOOCH_3 were distinctly separate from those in CH$_3$COOCH_3 or CH$_3$CH$_2$COOCH_3 (confirmed by spiking experiments).

All materials were used as purchased. Formic acid was 95–97% grade. The cyclooctadiene iridium(I) chloride was purchased from Strem Chemicals or synthesized according to literature procedure.[15]

Results and Discussion

The most unusual feature of the catalyst system is the requirement for a carboxylic acid solvent. In neat methyl formate essentially no reaction occurs even at 190 °C and in the presence of the most generally effective catalyst combination, (cyclooctadiene)iridium(I) chloride and methyl iodide (experiment II-1a). Upon addition of substantial quantities of acetic acid (experiment II-1b), reaction began immediately and proceeded smoothly. Addition of small amounts of carboxylic acid was insufficient for appreciable conversions even after 5 h of reaction time (experiment II-6). Mixtures of toluene and acetic acid as solvent gave conversions that were proportional to the amount of contained acetic acid (experiments II-3–5). In the experiments with high amounts of toluene, a purple

solid formed during the reaction which was IrI$_3$ according to elemental analysis. Otherwise, the solutions were orange to red in color and clear. Other carboxylic acids were acceptable as solvents, propionic or propionic and formic functioned quite well (experiments II-7 and II-8). Acetophenone was also unsatisfactory as a solvent (experiment II-2). Both types of solvents, polar and nonpolar, were found satisfactory in previous studies of "isomerizations" with other group 8 metals under carbon monoxide pressure, as well as neat solutions.[12,13]

Analysis of the reacting solutions during the early stages by VPC and ^{1}H NMR provided valuable information relative to the function of the carboxylic acid. It was evident that the first reaction to occur was transesterification of the methyl formate with the solvent carboxylic acid (eq 5). In solutions which were about 5 M methyl formate in propionic acid, the ratio of formic acid/methyl formate was approximately 2:1.

$$\text{HCOOCH}_3 + \text{RCOOH} \rightleftharpoons \text{HCOOH} + \text{RCOOCH}_3 \quad (5)$$
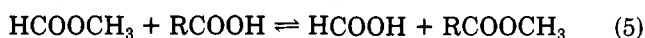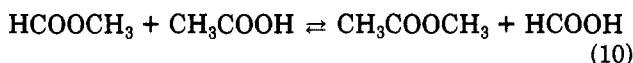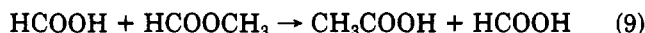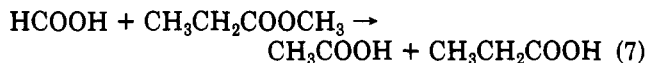
This finding raised the possibility that the active substrate was actually formic acid. This hypothesis was tested by employing a mixture of formic acid and methyl propionate instead of methyl formate (experiment II-9). This produced acetic acid and additional propionic acid. With the combination of formic acid and methyl alkanoate, acetophenone was quite satisfactory as a solvent (experiment II-10).

Most of the experiments utilized the combination of 95–97% formic acid and methyl ester in propionic acid, which made the analyses for product acetic acid more accurate. However, analyses for reactants and intermediates were complicated due to the large number of ester equilibria (eq 6, 10, and 11) and product-forming reactions (eq 7–9) involved. The reaction parameters and especially

$$\text{HCOOCH}_3 + \text{CH}_3\text{CH}_2\text{COOH} \rightleftharpoons$$
$$\text{HCOOH} + \text{CH}_3\text{CH}_2\text{COOCH}_3 \quad (6)$$

(15) Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth.* **1975**, *15*, 18.

$$HCOOH + CH_3CH_2COOCH_3 \rightarrow$$
$$CH_3COOH + CH_3CH_2COOH \quad (7)$$

$$HCOOH + CH_3COOCH_3 \rightarrow 2CH_3COOH \quad (8)$$

$$HCOOH + HCOOCH_3 \rightarrow CH_3COOH + HCOOH \quad (9)$$

$$HCOOCH_3 + CH_3COOH \rightleftharpoons CH_3COOCH_3 + HCOOH \quad (10)$$

$$CH_3COOCH_3 + CH_3CH_2COOH \rightleftharpoons$$
$$CH_3COOH + CH_3CH_2COOCH_3 \quad (11)$$

kinetic responses to reactant concentrations were complicated. The pertinent experiments are listed in Table III. Of special interest is the relationship of the reaction rates to formic acid concentration (experiments III-11–17; Figure 1). With the amount of methyl ester in large molar excess and held relatively constant, the initial rate was highly dependent on the formic acid concentration, approximately first order. These experiments were conducted with high levels of methyl iodide. The rate was independent of methyl ester concentration, except as it contributes to formic acid concentration by the ester interchange process (experiments III-1–10, Figure 2).

The rate of acetic acid formation is dependent on methyl iodide concentration at low and medium levels (0.01–0.15 M or 3–50 I/Ir) but shows small response at high levels (Figure 3). The initial form of the iodide is not critical, except that iodide salts are unsuitable. Initial aqueous HI is converted to methyl iodide, even before reaction temperature is reached. This observation is also important when considering the mechanism (vide infra). Other alkyl iodides are converted to methyl iodide after cycling through the synthesis steps. Branched iodides were converted to a greater extent than linear iodides. Iodide is necessary for the reaction to proceed (experiment IV-12).

The reaction will not proceed without a methoxy source; i.e., a stoichiometric reaction with generation of HI will not proceed to any significant extent (eq 12, experiment III-20).

$$CH_3I + HCOOH \xrightarrow{Ir} CH_3COOH + HI \quad (12)$$
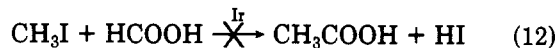
A reaction pathway which accommodates these facts in a manner consistent with demonstrated chemical phenomena is outlined in Scheme I. The species [LIrI] is a solvated iridium(I) complex. The oxidative addition of methyl iodide to iridium(I) is well documented, both for neutral and ionic species.[16] The slow step is probably the methyl migration (4 → 5) but could be the β-hydride elimination of step (3 → 4). This latter has been proposed as the rate-determining step in the decomposition of rhodium–formate[17] and iridium–formate[6b] species. The rate dependence of formic acid concentration would arise as a consequence of its competition with HI between species 2 and 3. This determines the concentration of the necessary intermediate 3 at any instance. The equilibrium M–X + OOCH⁻ → MOOCH + X⁻ has been proposed for M = Ir and X = Cl.[4b,c] The HI formed in the 2 → 3 conversion reacts immediately with the methyl ester of the solvent acid to produce methyl iodide and regenerate the solvent acid. This conversion is very fast as noted before and as confirmed by VPC evidence for free methyl iodide in all experiments except those with very low ratios of I/Ir. In the experiment with no methoxy acceptor (III-20), the initial buildup of HI either rapidly decreases the concen-
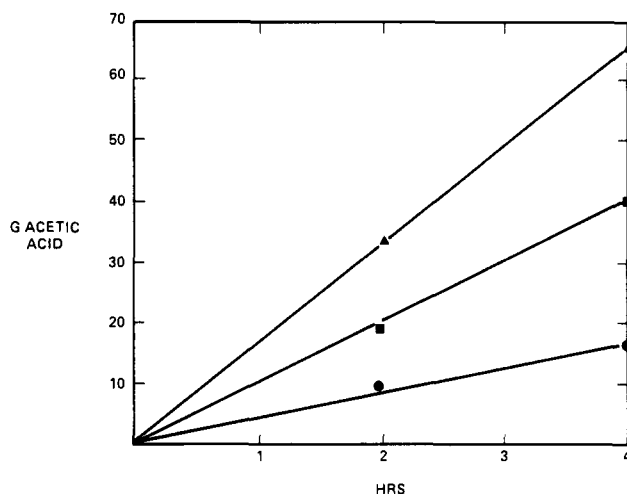

Figure 1. Rate of acetic acid formation as a function of formic acid concentration (Table III, experiments II-11–III-13): ●, 24 g of HCOOH; ■, 48 g of HCOOH; ▲ 72 g of HCOOH.
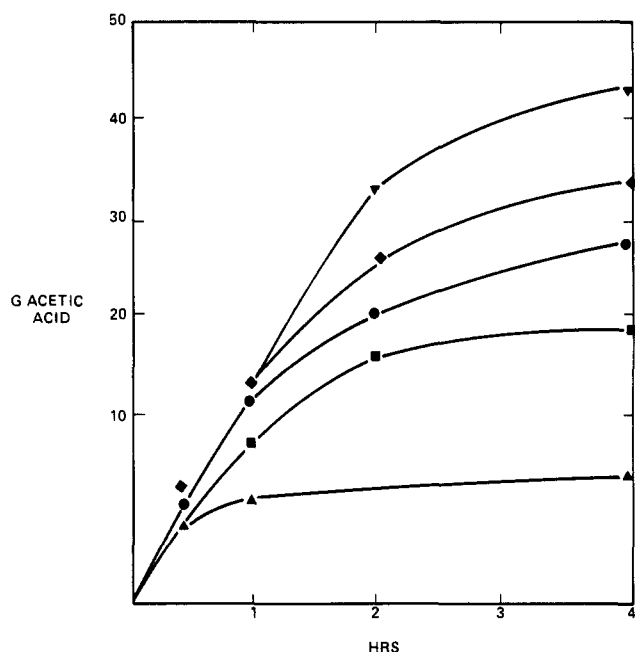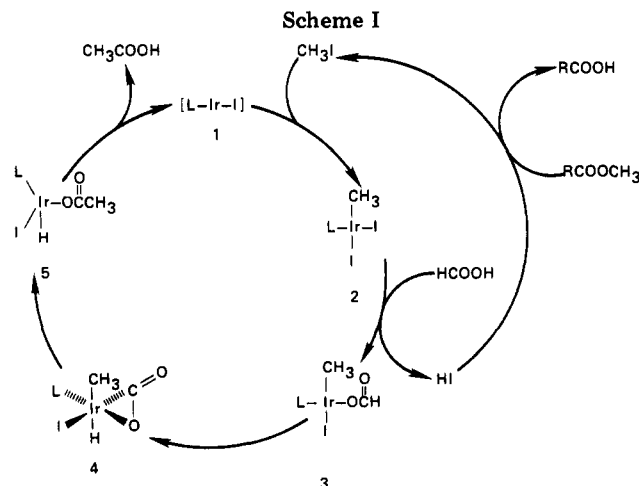

Figure 2. Rate of acetic acid formation as a function of methyl propionate concentration (Table III, experiments III-5, III-7–III-9): ▲, 22 g, ■, 44 g, ●, 55 g, ♦, 66 g and ▼, 88 g of methyl propionate.

Scheme I

(16) As an example, see: Forster, D. *J. Chem. Soc., Dalton Trans.* **1979**, 1639 and references therein.

(17) Strauss, S. H.; Whitmire, K. H.; Shriver, D. F. *J. Organomet. Chem.* **1979**, *174*, C59.

tration of 3 due to unfavorable equilibrium with 2 or the HI competes with CH₃I in oxidative addition of 1; the

Table III. Effect of Formic Acid and Methyl Ester Concentrations on Acetic Acid Formation

expt no.	reactants (g)	acetic acid produced, g			
		0.5 h	1.0 h	2.0 h	4.0 h
III-1[a]	$CH_3CH_2COOCH_3$ (44) HCOOH (72)			23.6	29.6 (99%)
III-2[a]	$CH_3CH_2COOCH_3$ (88) HCOOH (72)			38.3	54.6 (91%)
III-3[a]	$CH_3CH_2COOCH_3$ (132) HCOOH (72)			33.1	65.4 (73%)
III-4[b]	$CH_3CH_2COOCH_3$ (22) HCOOH (96)		11.8	14.8	15.9 (100%+)
III-5[b]	$CH_3CH_2COOCH_3$ (22) HCOOH (96)	7.6	14.8		13.6 (91%)
III-6[b]	$CH_3CH_2COOCH_3$ (33) HCOOH (96)	8.1	15.4	19.4	19.7 (88%)
III-7[b]	$CH_3CH_2COOCH_3$ (44) HCOOH (96)	10.2	16.9	25.3	28.1 (84%)
III-8[b]	$CH_3CH_2COOCH_3$ (55) HCCOH (96)	11.8	21.2	29.8	37.0 (99%)
III-9[b]	$CH_3CH_2COOCH_3$ (66) HCOOH (96)	12.4	22.3	36.7	43.8 (97%)
III-10	$CH_3CH_2COOCH_3$ (88) HCOOH (96)	11.7	21.6	42.7	52.7 (88%)
III-11[a]	$CH_3CH_2COOCH_3$ (132) HCOOH (24)			9.0	16.4 (55%)
III-12[a]	$CH_3CH_2COOCH_3$ (132) HCOOH (48)			19.1	41.1 (69%)
III-13[a]	$CH_3CH_2COOCH_3$ (132) HCOOH (72)			33.1	65.4 (73%)
III-14[b]	$CH_3CH_2COOCH_3$ (110) HCOOH (12)		5.7	4.5	6.0 (40%)
III-15[b]	$CH_3CH_2COOCH_3$ (110) HCOOH (21)		6.8	8.1	12.6 (48%)
III-16[b]	$CH_3CH_2COOCH_3$ (110) HCOOH (36)		7.6	10.9	23.7 (53%)
III-17[b]	$CH_3CH_2COOCH_3$ (110) HCOOH (48)		12.4	17.9	31.7 (53%)
III-18[b]	$CH_3CH_2COOCH_3$ (88) HCOOH (96)		28.3	49.1	53.2 (89%)
III-19[b]	$CH_3CH_2COOCH_3$ (88) HCOOH (96)	11.7	21.6	42.7	52.7 (88%)
III-20[c]	HCOOH (96)	...	...	...	0

[a] Reaction conditions were as follows: 0.5 g of $[Ir(COD)Cl]_2$, 18.2 g of CH_3I, 250 g of propionic acid as solvent; 185 °C reaction temperature. [b] Reaction conditions as follows: 0.5 g of $[Ir(COD)Cl]_2$, 22.7 g of CH_3I, 300 g of propionic acid as solvent; 180 °C reaction temperature. [c] Reaction conditions were as follows: 0.5 g of $[Ir(COD)Cl]_2$, 68.1 g of CH_3I, 300 g of propionic acid as solvent; 180 °C reaction temperature. No methyl ester present, hence no reaction.

oxidative addition of HI is nonproductive. It is known that HI undergoes oxidative addition much more rapidly than methyl iodide.[16]

The proposed coordinated carbon dioxide is similar to that demonstrated by Geoffroy and co-workers.[18] They showed that a rhenium complex with an O-bonded formate ligand reversibly expelled carbon dioxide through β-hydride elimination (eq 13). The reverse formate formation

$$[Re(OOCH)(diphos)_2] \rightleftharpoons [ReH(CO_2)(diphos)_2] \rightleftharpoons$$
$$[ReH(diphos)_2] + CO_2 \quad (13)$$

from complexed carbon dioxide and rhenium hydride must involve the migration of hydride to the carbon in the carbon dioxide. Since a methyl group migrates at least as readily as hydride in group 8 organometallic chemistry, the chemistry of the proposed 3 → 4 → 5 conversion is reasonable. Very recently it has been shown that the methyl group in $[CH_3W(CO)_5]^-$ in the presence of carbon dioxide forms $[CH_3COOW(CO)_5]^-$.[19] It is interesting to note that the reaction occurred under conditions in which carbon monoxide dissociation is not expected. Thus each step in

the catalytic cycle of Scheme I has established chemical precedent.

Addition of water to the reacting system gave unexpected results. The reaction of formic acid with methyl propionate was strongly inhibited by solutions of 1–4 mol of water in propionic acid. At 4 M H_2O concentration, no acetic acid was produced and the pressure in the autoclave rose to 1400 psi after 4 h at 180 °C. The gas was analyzed by mass spectrograph and analyzed 59% methane, 32% carbon dioxide and 5% hydrogen. At a 1 M concentration, the formation of acetic acid was slow (14 g after 2 h) and the pressure rose, but only to 400 psi (59% methane, 30% carbon dioxide). Smaller amounts of water had correspondingly less effect. No difference was detected between a reaction made completely anhydrous by addition of propionic anhydride and those utilizing the standard 95–97% formic acid. Solutions of the latter were 0.3 M. The reason for the dramatic effect of water is not known.[20]

(18) Roberts, D. R.; Geoffroy, G. L.; Bradley, M. G. *J. Organomet. Chem.* **1980**, *198*, C75.

(19) Darensbourg, D. J.; Rokicki, A. *J. Am. Chem. Soc.* **1982**, *104*, 349.

(20) A reviewer has noted that the effect of added water bears a strong resemblance to the work on iridium catalyzed methanol carbonylation[23] where high ionic iodide levels prevented methyl migration and instead diverted the catalysis along the pathway $CH_3OH + CO \rightarrow CH_4 + CO_2$. It was also suggested that another potential route for acetic acid formation in the (essentially) anhydrous system could involve formic acid decomposition to carbon monoxide and water.

Table IV. Effect of Iodide Promoter: Amount and Type

expt no.	reactants (g)	catalyst (g)	final iodide (g)	CH₃COOH produced, g
IV-1	CH₃CH₂COOCH₃ (67) HCOOH (96)	[Ir(COD)Cl]₂ (0.5) CH₃I (34.1)	CH₃I (31.1)	41.0[b]
IV-2	CH₃CH₂COOCH₃ (66) HCOOH (96)	[Ir(COD)Cl]₂ (0.5) CH₃I (11.4)	CH₃I (9.1)	41.4[b]
IV-3	CH₃CH₂COOCH₃ (66) HCOOH (96)	[Ir(COD)Cl]₂ (0.5) CH₃I (4.5)	CH₃I (2.9)	30.9[b,c]
IV-4	CH₃CH₂COOCH₃ (66) HCOOH (96)	[Ir(COD)Cl]₂ (0.5) CH₃I (2.3)	CH₃I (2.3)	21.7[b,d]
IV-5	CH₃CH₂COOCH₃ (66) HCOOH (96)	[Ir(COD)Cl]₂ (0.5) CH₃I (1.0)	CH₃I (1.1)	12.9[b,e]
IV-6[f]	CH₃CH₂COOCH₃ (88) HCOOH (96)	[Ir(COD)Cl]₂ (0.5) 55% aqueous HI (35)	CH₃I (18.7)	13.6
IV-7	CH₃CH₂COOCH₃ (88) HCOOH (96)	[Ir(COD)Cl]₂ (0.5) CH₃I (11.4) LiI (10.0)	CH₃I (11.7)	11.0[g]
IV-8	CH₃COOCH₃ (72) HCOOH (46)	[Ir(COD)Cl]₂ (0.5) (CH₃)₂CHI (50)	CH₃I (56.3) (CH₃)₂CHI (13.5)	90.7
IV-9[f]	CH₃COOCH₃ (72) HCOOH (72)	[Ir(COD)Cl]₂ (0.5) CH₃CH₂CH₂I (50)	CH₃I (19.0) CH₃CH₂CH₂I (23.7)	97.1
IV-10[h]	CH₃COOCH₃ (72) HCOOH (72)	[Ir(COD)Cl]₂ (0.5) CH₃CH₂CH(I)CH₃ (45)	CH₃I (30.1) CH₃CH₂CH(I)CH₃ (8.2)	91.5
IV-11[h]	CH₃COOCH₃ (72) HCOOH (72)	[Ir(COD)Cl]₂ (0.5) (CH₃)₃CI (50)	CH₃I (35.1)	78.7
IV-12[i,j]	HCOOCH₃ (90)	[Ir(COD)Cl]₂ (0.5)	...	

[a] Experimental conditions: 4 h reaction time; 300 g of propionic acid as solvent; 180 °C reaction temperature. [b] The amount of acetic acid was measured after 0.5, 1, and 2 h. That found at the respective times was (IV-5) 5.3, 5.4, 7.5, (IV-4) 5.1, 7.4, 11.8, (IV-3) 6.6, 9.6, 17.4, (IV-2) 11.6, 17.4, 32.4, (IV-1) 12.5, 23.1, 35.3. [c] Product contained 11.6 g of unreacted methyl propionate. [d] Product contained 12.9 g of unreacted methyl propionate. [e] Product contained 32.7 g of unreacted methyl propionate and 8.4 g of methyl formate. [f] The HI was transformed to CH₃I before the reaction temperature was reached. The low yield of acetic acid was caused by the water inhibition. [g] The pressure rose to 6.1 MPa during the reaction. [h] Samples were taken at 160 °C and again upon reaching 180 °C. The n-propyl iodide did not convert to methyl iodide until 1 h at 180 °C. The sec-butyl iodide was converted upon reaching 180 °C but not at 160 °C. The tert-butyl iodide was 50% converted at 160 °C. [i] Reaction temperature 200 °C; solvent propionic acid, 250 g. [j] Black precipitate formed during the reaction.
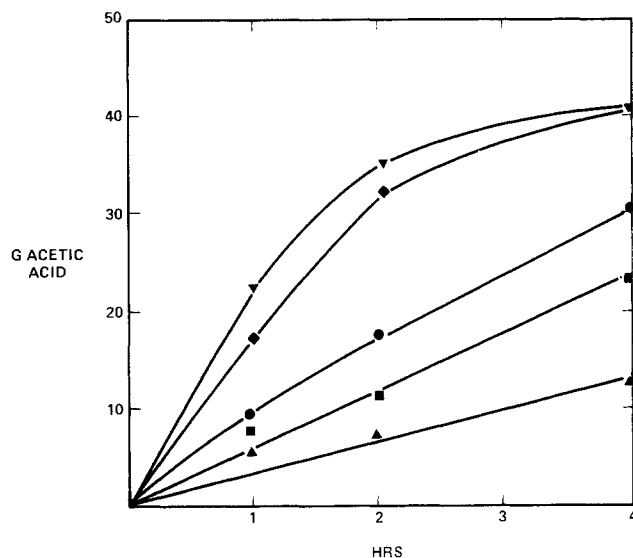
Figure 3. Rate of acetic acid formation as a function of methyl iodide concentration (Table IV, experiments IV-1–5): ▲, 1 g of CH₃I; ■, 2.3 g of CH₃I; ●, 4.5 g of CH₃I; ♦, 11.4 g of CH₃I; ▼, 34.1 g of CH₃I.

The "isomerization" was also applicable to other formate esters. Ethyl formate (100 g) was transformed to propionic acid (41.2 g) when heated to 200 °C for 4 h in acetic acid (250 g) in the presence of [Ir(COD)Cl]₂ (0.5 g) and CH₃I (45.4 g). In a similar manner, isopropyl acetate (153 g) and formic acid (75 g) in acetic acid (200 g) and in the presence of [Ir(COD)Cl]₂ (0.5 g) and isopropyl iodide (36 g) formed mixture of butyric acids (35.6 g). The carboxylic acid formation from the higher homologues was less facile than the acetic acid synthesis from either methyl formate or
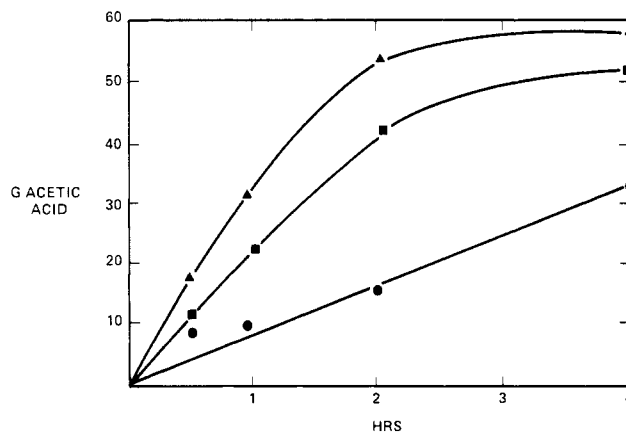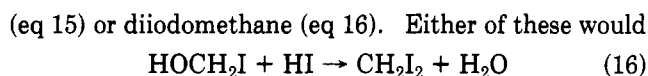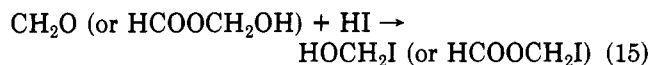

Figure 4. Rate of acetic acid formation as a function of iridium concentration: ●, 250 ppm of Ir; ■, 640 ppm of Ir; ▲, 1000 ppm of Ir.
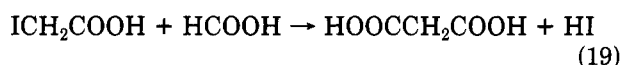
methyl propionate and formic acid. Other group 8 metals were not effective catalysts under these conditions. Ruthenium(III) acetylacetonate and methyl iodide did not catalyze the reaction of formic acid and methyl propionate in propionic acid. After 4 h at 180 °C the yield of acetic acid was <4%. Rhodium as the (cyclooctadiene)rhodium(I) chloride dimer plated out during a similar reaction. With the iridium catalyst, the reaction was approximately first order in Ir.

Formaldehyde as Reactant. Formaldehyde is an interesting substrate for the formic acid reaction. Several possibilities could occur. It could exist as a pseudo ester (eq 14) which could possibly form a hydroxymethyl iodide

$$CH_2O + HCOOH \rightarrow HCOOCH_2OH \qquad (14)$$

$$CH_2O \ (or \ HCOOCH_2OH) + HI \rightarrow$$
$$HOCH_2I \ (or \ HCOOCH_2I) \quad (15)$$

(eq 15) or diiodomethane (eq 16). Either of these would

$$HOCH_2I + HI \rightarrow CH_2I_2 + H_2O \qquad (16)$$

produce interesting products under the reaction conditions. Reacting as hydroxymethyl iodide, glycolic acid would be produced (eq 17). Reacting as diiodomethane, the product could be either iodoacetic acid (eq 18) or malonic acid (eq 19).

$$HOCH_2I + HCOOH \rightarrow HOCH_2COOH + HI \quad (17)$$

$$ICH_2I + HCOOH \rightarrow ICH_2COOH + HI \quad (18)$$

$$ICH_2COOH + HCOOH \rightarrow HOOCCH_2COOH + HI$$
$$(19)$$
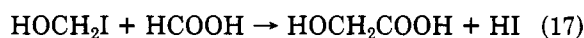
When trioxane was treated with formic acid under typical reaction conditions, none of the products according to the above reactions were detected. At 180 °C, almost no reaction occurred. In the VPC analysis of the product, a very large peak was observed at very short retention times (Poropak T column, thermal conductivity detector, column temperature 170 °C), even shorter than that for water or methyl formate. This was presumed to be monomeric formaldehyde. This point was not proved by further analyses. At a reaction temperature of 205 °C, this peak disappeared during the first 2 h, and reaction products appeared. Typical results are shown in Figure 5. Methyl formate is seen in the first hour of reaction, in increasing amounts, and then drops to negligible quantities after 3 h. Methyl propionate increased more rapidly in the same time frame and also decreased to small quantities at the end of the 4-h period. On the other hand, acetic acid was present in relatively small amounts until the later stages of the reactions and was present in high yields at the end of the reaction. Methyl iodide was seen in all stages.

It was concluded that the reaction followed a new pathway. The first reaction is a Tischenko-like condensation of formaldehyde to form methyl formate (eq 20).

$$2CH_2O \rightarrow HCOOCH_3 \qquad (20)$$

This type of reaction has been noted to proceed with rhodium[21] or copper[22] catalysts. This is substantiated by the observation of substantial quantities of methyl formate
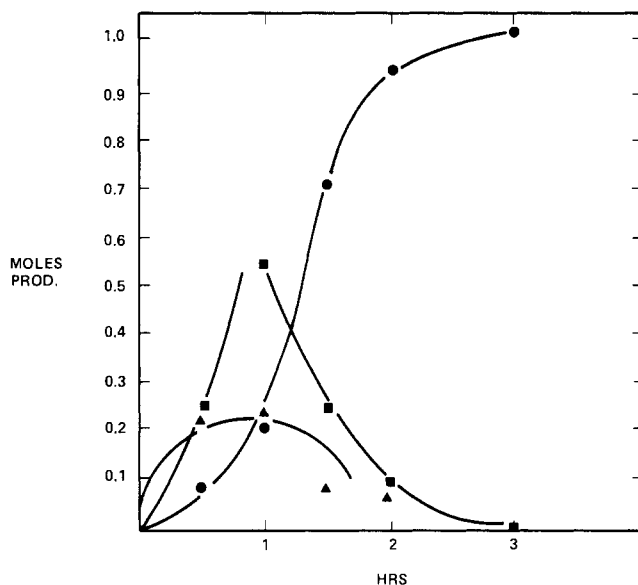
Figure 5. Intermediates in the formation of acetic acid from formaldehyde: ▲, methyl formate; ■, methyl propionate; ●, acetic acid.

early in the reaction, followed by acetic acid late in the reaction. The amount of methyl formate is much larger than would be seen if methyl propionate was formed initially by another route, and then trans-esterification occurred to form methyl formate. In fact, the opposite occurs. The acetic acid could be formed by decarboxylation of malonic acid as formed in eq 19, but that would not account for the methyl esters. Also the intermediate promoter would not be methyl iodide, which was seen throughout the reaction. Thus the Tischenko route is the most likely.

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(22) Goeden, G. V.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 7354.

(23) Forster, D. *J. Chem. Soc., Dalton Trans.* **1979**, 1639.