Homogeneous Catalysis of the Reppe Reaction with Iron Pentacarbonyl: The Production of Propionaldehyde and 1-Propanol from Ethylene

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Abstract: The Reppe hydroformylation of ethylene to produce propionaldehyde and 1-propanol in basic solutions containing $Fe(CO)_5$ as a catalyst has been studied under carefully controlled conditions at temperatures ranging from 110 to 140 °C. Propionaldehyde is the principal product formed when NaOH is used as the base. The rate of reaction is found to increase with ethylene concentration and is second order with respect to $Fe(CO)_5$. The reaction is inhibited by CO. The increase in reaction rate with temperature corresponds to an activation energy of 31 kcal/mol. Infrared spectra indicate that $HFe(CO)_4^-$ and $Fe(CO)_5$ are present in the solution phase under reaction conditions. The experimental results are shown to be consistent with a mechanism in which the rate-determining step involves a binuclear iron carbonyl derivative. The substitution of $(C_2H_5)_3N$ for NaOH facilitates the reduction of propionaldehyde to form 1-propanol but results in a slower rate for the overall reaction.

In 1953, Reppe and Vetter[1] first reported that iron carbonyl dissolved in an aqueous solution of base was a catalyst for a reaction in which an olefin combines with carbon monoxide and water to form an alcohol having an additional carbon atom as shown in eq 1 with ethylene as the olefin substrate. Aside from

$$CH_2{=}CH_2 + 3CO + 2H_2O \rightarrow CH_3CH_2CH_2OH + 2CO_2 \quad (1)$$

any commercial importance,[2,3] this reaction has been of interest to chemists because it represents an example in which water, in conjunction with carbon monoxide, is the sole source of hydrogen for an "OXO" type reaction involving the reductive addition of carbon monoxide to an olefin.[3]

Later investigations by Pettit and co-workers[4,5] showed that this reaction does not incorporate a reduction step utilizing molecular hydrogen produced by the $Fe(CO)_5$ catalyzed water gas shift reaction. They further showed that aldehydes as well as alcohols are present in the product mixture at early stages of the reaction, suggesting that the reaction proceeds in two stages, the first being a hydroformylation reaction producing an aldehyde one carbon larger than the parent olefin with the second being the reduction of this aldehyde to produce the final product, an alcohol. Viewed in this context, eq 1 becomes

$$CH_2{=}CH_2 + 2CO + H_2O \rightarrow CH_3CH_2CHO + CO_2 \quad (2a)$$

$$CH_3CH_2CHO + CO + H_2O \rightarrow CH_3CH_2CH_2OH + CO_2 \quad (2b)$$

The standard free energies for reactions 2a and 2b are both strongly negative, having values of $\Delta G°_{298} = -19.3$ and -12.1 kcal, respectively. Thus reactions 2a and 2b can be considered as two thermodynamically independent reactions both of which utilize an equimolar mixture of CO and H_2O rather than H_2 as the reducing agent.[6]

It is generally agreed that the iron-containing compound responsible for catalyzing reactions 2a and 2b is the hydridotetracarbonylferrate anion, $HFe(CO)_4^-$, or a species derived from this anion, although the exact nature of the catalytically active species is open to some question. For example, while the ability of $HFe(CO)_4^-$ to reduce aldehydes under stoichiometric as well as catalytic conditions (i.e., reaction 2b) has been demonstrated,[4,5,7,8] both $H_2Fe(CO)_4$[4,5] and a dimer of $HFe(CO)_4^-$[9] have been postulated to be the active species involved in catalyzing reaction 2a above.

The work reported here was undertaken with the expectation that a thorough study of the kinetics of the Reppe reaction with the simplest possible substrate, ethylene, might serve to identify the catalytic pathway by which this reaction proceeds and by so doing remove any ambiguity with regards to the role played by the hydridotetracarbonylferrate ion in the overall reaction.

Experimental Section

The kinetic experiments were carried out with use of using small stainless steel (type 304) autoclaves having an internal volume of 700 mL. The autoclaves, having been charged with a particular catalyst solution and gas mixture of interest, were mounted vertically in electrically heated ovens, each having a magnetic stirrer built onto its base. An ordinary 1-in.-long Teflon-coated magnetic stirring bar was used to stir the liquid phase within each autoclave. Each oven contained a 576-W heater which was controlled by a proportional controller (Love Controls Model 71) with a thermocouple sensor mounted in a thermocouple well extending into the interior of the autoclave. After a short warmup period (~25 min), temperatures within an autoclave could be maintained constant to within ±1 °C as determined by an Omega Engineering Inc. Model 250 T digital thermocouple read-out meter. The total pressure within each autoclave was monitored with a Matheson Model 63 test gauge (0-3000 psig), accurate to 0.25% of full scale, which was attached to each autoclave through the closure at the top.

A Fisher Model 1200 gas partitioner with a 6.5-ft. 80–100-mesh Columnpak PQ column followed by a 11-ft 13× molecular sieve column was used with helium as a carrier gas at 50 °C to analyze for the principal gases of interest (CO, C_2H_4, and CO_2) extracted from the bomb. The small amounts of hydrogen, produced by the water gas shift reaction occurring as a side reaction during these experiments, was monitored with a Varian Model 920 gas chromatograph with a 8-ft. column of 13× molecular sieve with argon as a carrier gas at 50 °C. A Varian CDS-111

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(1) Reppe, W.; Vetter, H. *Liebigs Ann. Chem.* **1953**, *582*, 133.

(2) A brief description of a commercial process based on the Reppe reaction can be found: *Hydrocarbon Process.* **1967**, *46*, 154.

(3) Publications and patents concerned with the Reppe synthesis of alcohols prior to 1977 are reviewed in the following: Wender, I.; Pino, P. *Organic Synthesis via Metal Carbonyls*; Wiley-Interscience: New York, 1977; Vol. 2.

(4) Kang, H.; Mauldin, C. H.; Cole, T.; Slegir, W.; Cann, K.; Pettit, R. *J. Am. Chem. Soc.* **1977**, *99*, 8323.

(5) Pettit, R.; Mauldin, C. H.; Cole, T.; Kang, H. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 151.

(6) The assumption that reactions 2a and 2b operate independently is supported by the observation by Pettit[4] that while aldehydes are readily reduced by aqueous solutions of $Fe(CO)_5$ and base under CO pressure over a wide range of basicities, the uptake of olefin by such solutions is very sensitive to pH and does not occur at pH values greater than 10.7.

(7) Sternberg, H. W.; Markby, R.; Wender, I. *J. Am. Chem. Soc.* **1956**, *78*, 5704.

(8) Markó, L.; Radhi, M. A.; Ötvös, I. *J. Organomet. Chem.* **1981**, *218*, 369.

(9) Wender, I.; Sternberg, H. W.; Friedel, R. A.; Metlin, S. J.; Markby, R. Ed. *The Chemistry and Catalytic Properties of Cobalt and Iron Carbonyls*; U.S. Bureau of Mines: Washington, D.C., 1962; Bulletin 600.

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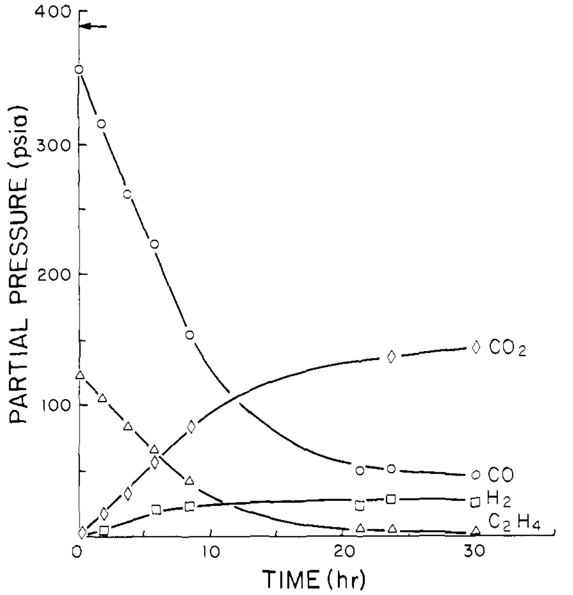

Figure 1. Partial pressures of CO, C_2H_4, CO_2, and H_2 as a function of time. Catalyst solution: $Fe(CO)_5$ (2.2 mmol), KOH (36 mmol), 200 mL (25% H_2O, 75% CH_3OH v/v). Temperature: 120 °C. Loading pressure of CO corrected to 120 °C: 390 psia (←).

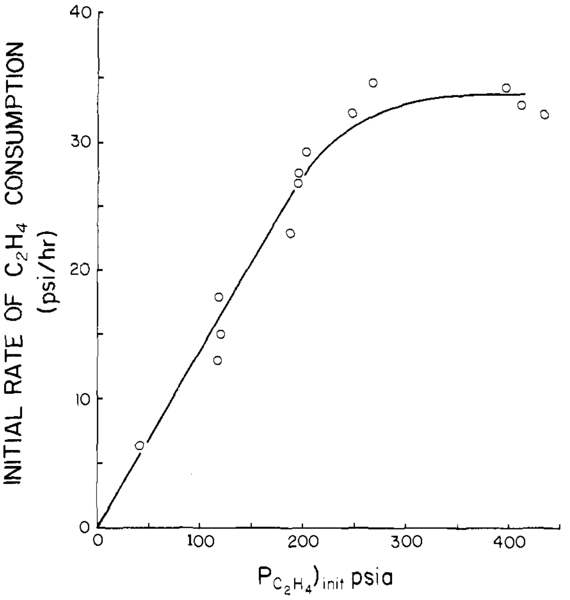

Figure 3. Initial rate of ethylene consumption as a function of initial ethylene pressure. Catalyst solution: $Fe(CO)_5$ (4.5 mmol), KOH (36 mmol), 200 mL (25% H_2O, 75% CH_3OH v/v). Temperature: 110 °C. Initial partial pressure of CO: 355 ± 12 psia.

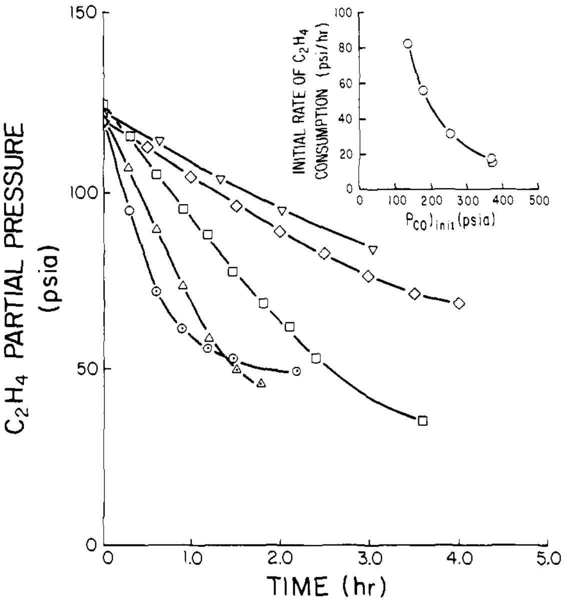

Figure 2. Partial pressure of ethylene as a function of time showing the variation in rate of consumption with carbon monoxide pressure. Catalyst solution: $Fe(CO)_5$ (4.5 mmol), KOH (36 mmol), 200 mL (25% H_2O, 75% CH_3OH v/v). Temperature: 110 °C. Initial partial pressure of C_2H_4: 122 ± 2 psia. ○, $P(CO)_{init}$ = 138 psia; △, $P(CO)_{init}$ = 177 psia; □, $P(CO)_{init}$ = 247 psia; ◇, P_{init} = 369 psia; ▽, $P(CO)_{init}$ = 367 psia. (Symbols with solid dots correspond to conditions in which the partial pressure of carbon monoxide has become less than 50 psia leading to decomposition of the $Fe(CO)_5$ catalyst system to produce ferrous carbonate.)[11] Inset: Initial rates of ethylene consumption as a function of initial CO partial pressure.

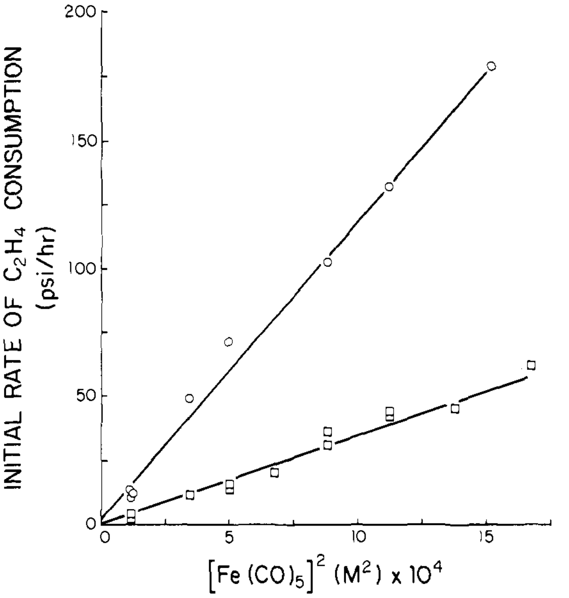

Figure 4. Initial rate of ethylene consumption as a function of formal concentration of $Fe(CO)_5$. Catalyst solution: $Fe(CO)_5$ (variable), KOH (36 mmol), 200 mL (25% H_2O, 75% CH_3OH v/v). Temperature: 110, 120 °C. Initial partial pressure of CO: 361 ± 8 psia. Initial partial pressure of C_2H_4: 120 ± 4 psia. ○, T = 120 °C; □, T = 110 °C.

digital integrator was used to collect the output of each gas partitioner.

Gas sampling was accomplished by releasing samples of the gas mixture from the interior into a sample chamber which uses a small balloon to maintain a low positive pressure against a septum. This sample was purged three times prior to removing a sample for inspection on the gas partitioners by means of a Pressure-Lok syringe.

The compositions of the gas mixtures, expressed in terms of partial pressure, were calculated according to the following procedure. The composition of the initial loading of Ar, CO, and C_2H_4 is first determined at room temperature prior to heating the autoclave. The partial pressure of Ar computed from these data and the gauge pressure according to Dalton's law is then corrected to the elevated temperature at which the kinetic data are subsequently obtained by using the ideal gas approximation. This allows partial pressures of the gases of interest, CO, C_2H_4, and CO_2, to be computed directly by the digital integrator during the course of the experiment. The average experimental error in partial pressure derived from repetitive measurements is found to be ±2 psia.

The gases used in these experiments were CP grade or the equivalent having quoted purities of 99.5% or better. Fisher certified ACS grade methanol and laboratory distilled water were used to make up the solvent mixture (25% H_2O–75% methanol by volume) used in these experiments. Fisher Certified ACS grade potassium hydroxide and distilled triethylamine purchased from J. T. Baker Chemical Co. were used as bases. The iron pentacarbonyl was purchased from Alfa Division of Ventron Corp. It had a quoted purity of 99.5% and was used with no subsequent purification.

Results and Discussion

Data obtained from these experiments are shown in Figures 1–5. The familiar units of "pounds per square inch" rather than

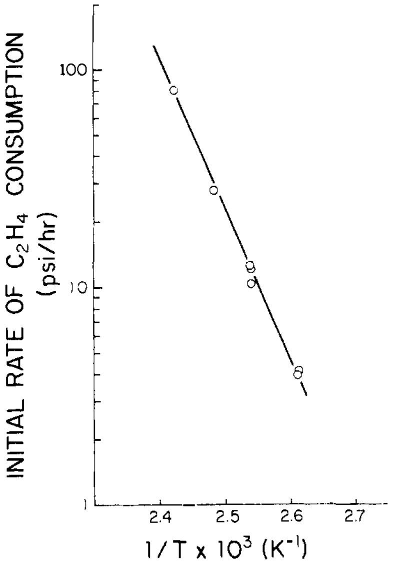

Figure 5. Initial rate of ethylene consumption as a function of temperature. Catalyst solution: $Fe(CO)_5$ (2.2 mmol), KOH (36 mmol), 200 mL (25% H_2O, 75% CH_3OH v/v). Temperatures: 110, 120, 130, and 140 °C. Initial partial pressure of CO: 360 ± 6 psia. Initial partial pressure of C_2H_4: 116 ± 6 psia.

SI units have been used to represent partial pressures primarily for convenience. However, an additional benefit is derived from this choice of units. The liquid loading of the alcohol–water solvent mixture was set at 200 mL for each experiment leaving a gas volume of 500 mL within the autoclaves. A consequence of this is that over the temperature range of these experiments, a pressure increment of 1 psi closely corresponds to the consumption or production of 1 mmol of gas and vice versa. Thus, to a good approximation the ordinates of Figures 1–5 correspond numerically to mmol of gas produced or consumed as well as partial pressure.[10]

The kinetics experiments reported here for the most part utilize KOH as a base. In a typical experiment, the autoclave is loaded with 200 mL of the methanol–water solution containing dissolved KOH and $Fe(CO)_5$ and is charged with a CO, C_2H_4, Ar mixture of the appropriate composition. After the exact gas composition is determined initially at room temperature, the autoclave is heated rapidly with stirring during which time the gauge pressure rises due to the thermal expansion of the gases and the increasing vapor pressure of the solvent mixture. As might be expected, the system exhibits much the same behavior as found in earlier studies of the $Fe(CO)_5$-base catalyzed water-gas shift reaction,[11] namely that when the temperature reaches ~80 °C the pressure ceases to rise briefly due to the reaction of CO with base to produce potassium formate. After this interruption, the pressure again rises until the temperature becomes constant. About this time CO_2 production is first noted, indicating the onset of the Reppe reaction.

Figure 1 shows the results obtained in a typical experiment such as described above. Three important features of the Reppe reaction are illustrated in this experiment. First, inspection of the data confirms that the reaction is indeed catalytic with respect to both $Fe(CO)_5$ and base in that approximately 125 mmol of ethylene, which serves as the limiting reagent in this case, is consumed in a system containing 2.2 mmol of $Fe(CO)_5$ and 36 mmol of KOH.

Second, the partial pressure of CO at the beginning of the reaction is 358 psia. The loading pressure of CO for this reaction was 289 psia at 18 °C, which when corrected to 120 °C corresponds to 390 psia as indicated by the arrow on the *Y* axis of Figure 1. The discrepancy between these two pressures, (390 − 358 = 32 psia) corresponds to a loss of 34 mmol of CO, indicating that virtually complete conversion of hydroxide ion (36 mmol) to formate ion, according to eq 3, has occurred prior to the onset of the Reppe reaction.

$$CO(g) + OH^- \rightarrow HCO_2^- \qquad (3)$$

Third, the initial slopes of the curves for the various gases correspond to −24 and −10 psi/h for CO and C_2H_4 and +10 and +3 psi/h for CO_2 and H_2, respectively. It is reasonable to assume that the small amount of H_2 produced is formed through the water gas shift reaction which is seen from the 1:1 stoichiometry of eq 4 to require an equal rate of consumption of CO. Thus, one estimates that the carbon monoxide consumption rate associated

$$CO(g) + H_2O(l) \rightarrow H_2(g) + CO_2(g) \qquad (4)$$

with the uptake of ethylene is 24 − 3 = 21 psi/h, which corresponds to a mole ratio of 21 psi (CO)/h:10 psi (C_2H_4)/h or 2.1 mol of CO/mol of C_2H_4. It is clear from this that the dominant process occurring in the early stages of this reaction is the production of propionaldehyde (eq 2a), which requires a 2:1 mol ratio of CO to C_2H_4 rather than the 3:1 stoichiometry necessary in order for propanol to be formed.[12] This, of course, provides quantitative support for the conclusion drawn earlier by Pettit[4,5] and others[13] that alcohol production by the Reppe reaction proceeds by two consecutive and independent reactions as shown in eq 2a and 2b. In some instances trace quantities of ethane rather than hydrogen appear in the gas mixture, particularly in the later stages of the reaction. However, the side reaction responsible for this reduction of ethylene proceeds quite slowly and in the most extreme instances accounts for less than 8% of total ethylene consumption. It follows, therefore, that under the conditions of these experiments, the determination of the rate of consumption of ethylene in the early stages of the reaction provides information concerning the kinetics of the hydroformylation reaction, eq 2a above.[14]

The previous discussion has focussed primarily on the operational characteristics of the Reppe reaction carried out in a closed system. They are found to be quite similar to those of the $Fe(CO)_5$-catalyzed water gas shift reaction.[11] Turning to the kinetics proper, one sees that apart from solvent composition which is not considered here,[15] there are six variables that can in principle affect the rate of the Reppe reaction. They are (1) partial pressure of carbon monoxide, (2) partial pressure of ethylene, (3) catalyst concentration, (4) temperature, (5) base concentration/pH, and (6) the nature of the base. The effect of each of these variables on the kinetics of the Reppe reaction has been examined separately.

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(10) Strictly speaking, an increment of 1 psia corresponds to 1.08, 1.05, 1.03, and 1.00 mmol at temperatures of 110, 120, 130, and 140 °C, respectively. These more accurate values are used in relevant discussions within the text.

(11) King, A. D., Jr.; King, R. B.; Yang, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 1028.

(12) Other experiments of this study incorporating varying amounts of $Fe(CO)_5$, CO, and C_2H_4 yielded similar results with mole ratios of CO to C_2H_4 varying between 2.0 and 2.4 in a random fashion. The conclusion that propionaldehyde is a major product in this reaction was confirmed in a most obvious fashion by a pungent fruity odor characteristic of propionaldehyde which escaped upon opening the autoclaves at the conclusion of the various experiments.

(13) In this original paper (ref 1a) Reppe and Vetter suggested that a carbonylation followed by a reduction as shown in eq 2a and 2b represented a logical course to expect the Reppe reaction to follow. This view has been repeated in subsequent work (ref 7). However, neither group demonstrated the presence of aldehydes in the reaction mixture as was shown by Pettit (ref 4 and 5).

(14) Although the contents of the autoclave constitute a closed system, the overall mechanism of this reaction of necessity includes kinetic steps involving the transfer of CO, C_2H_4, and CO_2 across the gas–liquid interface. Consequently, preliminary kinetic studies were performed to determine the effect of stirring speed on the rate of ethylene consumption. It was found that a rate of rotation for the stirring bar (determined stroboscopically) of 500 rpm or greater provided sufficient agitation to prevent mass transfer effects from influencing the kinetics of the reaction. All kinetic data reported in this paper were taken with stirrer speeds between 500 and 1000 rpm.

(15) As noted earlier, a constant liquid loading of 200 mL of a 25% H_2O–75% methanol mixture was used in every experiment described here. Thus, water is present in a large excess in comparison with the other reactants in these experiments. No attempt has been made to study the effects of water concentration or solvent dielectric constant on the rate of the Reppe reaction.

Table I. The Effect of Gas Partial Pressure on the Initial Rate of Consumption of Ethylene by the Reppe Reaction[a]

$P(CO)_{init}$ (psia)	$P(C_2H_4)_{init}$ (psia)	rate (psi/h)
138	120	83
177	122	55
247	125	32
367	122	13
369	120	15
383	41	6
345	113	18
360	187	23
350	194	28
360	196	27
343	200	29
353	245	32
340	266	35
348	395	34
341	409	33
353	433	32

[a] Catalyst solution: Fe(CO)$_5$ (4.5 mmol), KOH (36 mmol), 200 mL (25% H_2O, 75% CH_3OH v/v). Temperature: 110 °C.

Figure 2 shows the results of a series of experiments in which the rate of ethylene consumption was measured at a series of different CO pressures holding all other variables constant. The catalyst solution used in these experiments consisted of 0.6 mL (4.5 mmol) of Fe(CO)$_5$ and 2.02 g (36 mmol) of KOH dissolved in 200 mL of the 25% H_2O–75% methanol mixture used in all of these experiments. Gas mixtures were chosen such that the partial pressure of ethylene was approximately 120 psia at the onset of each reaction which was carried out at 110 °C. The ethylene pressure decreases nearly linearly with time in the early stages of this reaction thus permitting precise (±2 psi/h) values for initial rates of ethylene consumption to be obtained from linear terms of second- or third-order polynomials fit to the pressure–time data with standard regression methods. Initial rates of ethylene consumption obtained from these experiments are listed as the first five entries of Table I and are shown plotted as a function of measured CO partial pressure in the inset of Figure 2. It is obvious from these data that carbon monoxide has an inhibitory effect upon the Reppe reaction.

It is considerably more difficult to control partial pressures of CO than those for ethylene in these experiments, primarily because of CO absorption to produce formate ion. Nevertheless, inspection of Table I shows that the fourth through final entries represent rates of ethylene consumption taken at various ethylene pressures with the initial CO pressure being approximately constant. These data are represented graphically in Figure 3. Although there is considerable scatter among these data, due in part to the poor control over the initial CO pressure, it is clear that the rate of reaction increases linearly with ethylene pressure in the low-pressure regime but exhibits saturation at ethylene pressures exceeding 250 psia.

Two series of kinetic studies were carried out, one at 110 °C and the other at 120 °C, to determine the variation in rate of reaction with catalyst concentration. The results are listed in Table II. These data are shown plotted as a function of the square of iron pentacarbonyl concentration in Figure 4. The linearity of each plot clearly indicates that the reaction is second order with respect to catalyst concentration.

The last two entries of Table II can be combined with the other appropriate ([Fe(CO)$_5$] = 0.011 M) data of this table allowing one to construct the Arrhenius plot shown in Figure 5. The straight line fitted to the data of Figure 5 corresponds to an activation energy of 31 kcal/mol (130 kJ/mol).

A series of experiments was carried out in an attempt to use IR spectroscopy and pH measurements to characterize the catalyst solution as it functions under typical reaction conditions (T = 110 °C, $P(CO)_{init}$ = 160 psia, $P(C_2H_4)_{init}$ = 110 psia). To do this, the closure of one autoclave was modified to allow small (3 cm^3) liquid samples to be withdrawn during the course of the reaction. The samples thus obtained were allowed to cool under N_2 prior to subsequent measurements. The pH of each sample was determined with use of a standard glass microelectrode.[16] The results obtained with two solutions containing 2.2 and 7.4 mmol of Fe(CO)$_5$ dissolved in the usual base–alcohol–water mixture (36 mmol KOH, 200 mL of 25% H_2O–75% CH_3OH v/v) were found to be the same. In each case the first sample obtained just prior to the stabilization of temperature and onset of reaction[17] had a pH of 12 and showed one intense band at 1900 cm^{-1} due to HFe(CO)$_4^-$. Samples taken periodically at later times during the course of the reaction had effectively constant pH values falling within the range pH = 8.7–8.9. Infrared spectra of these latter samples revealed the presence of two bands having comparable intensities, one at 1900 cm^{-1} corresponding to HFe(CO)$_4^-$ and the other at 2000 cm^{-1} due to Fe(CO)$_5$. In addition, IR spectral measurements were carried out directly on a catalyst solution (4.5 mmol of Fe(CO)$_5$ in 200 mL of 25% H_2O–75% CH_3OH solution containing 36 mmol of KOH) operating under slightly different conditions ($P(CO)_{init}$ = 350 psia, ($P(C_2H_4)_{init}$ = 180 psia, T = 110 °C) with use of a autoclave–infrared cell (spectroclave) developed in this laboratory.[18] These experiments yielded substantially identical results, namely that while only a single absorption band due to HFe(CO)$_4^-$ at 1900 cm^{-1} can be found in the catalyst solution prior to reaction, two bands arising from Fe(CO)$_5$ (2000 cm^{-1}) and HFe(CO)$_4^-$ (1900 cm^{-1}) are found in the catalyst solution during the course of reaction. None of the IR spectra recorded in either of these experiments showed any measurable absorption in the immediate vicinity of 1940 cm^{-1}, a frequency at which the dinuclear anion HFe$_2$(CO)$_8^-$ exhibits a strong absorption band.[19]

In general, the experiments described above indicate that the Reppe hydroformylation reaction 2a proceeds in an environment quite similar to that found when Fe(CO)$_5$ is used to catalyze the water gas shift reaction in basic alcohol–water solutions.[11] This suggests that the Reppe reaction and the homogeneously catalyzed water gas shift reaction may utilize common iron-containing intermediates in their respective catalytic cycles, even though the kinetics are quite different for the two reactions, the reaction being second order with respect to catalyst for the Reppe reaction and first order for the water gas shift reaction.[11]

Since HFe(CO)$_4^-$ is the only iron carbonyl derivative found in the infrared spectra of the reaction mixture prior to the onset of the hydroformylation reaction, it is clear that the Fe(CO)$_5$ has been totally converted to the hydridotetracarbonylferrate anion during the initial warm up period according to the reaction

$$OH^- + Fe(CO)_5 \rightarrow HFe(CO)_4^- + CO_2 \qquad (5)$$

Furthermore, the fact that infrared absorption bands due to Fe(CO)$_5$ appear in the reaction mixture only after the uptake of ethylene has begun suggests that Fe(CO)$_5$ is a product of the catalytic cycle and may function as a recycling catalyst in the series of reactions by which the Reppe hydroformylation proceeds.

While the experimental data presented here do not provide an unambiguous basis for formulating a detailed mechanism for this reaction, the fact that the overall rate for this hydroformylation reaction is second order with respect to iron strongly suggests that the rate-determining step of this reaction either (i) involves the reaction of a binuclear iron carbonyl derivative or (ii) consists of a reaction analogous to that reported by Barborak and Cann[20] in which a coordinately unsaturated monoiron acyl anion, which

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(16) Pearson and Mauermann (Pearson, R. G.; Mauermann, H. *J. Am. Chem. Soc.* **1982**, *104*, 500) have noted that a glass electrode provides accurate pH readings for methanol–water mixtures such as used here.

(17) Gas analyses performed concurrently with the liquid sampling in the period prior to the stabilization of temperature indicated a gradual decrease in CO pressure, presumably due to a slow reaction with residual hydroxide ion, while the partial pressure of ethylene remained constant. The "onset of reaction" referred to in these experiments is defined to be the point in time at which the ethylene partial pressure begins to fall.

(18) King, R. B.; King, A. D., Jr.; Iqbal, M. Z.; Frazier, C. C. *J. Am. Chem. Soc.* **1978**, *100*, 1687.

(19) Collmann, J. P.; Finke, R. G.; Matlock, P. L.; Wahren, R.; Komoto, R. G.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 1119.

(20) Barborak, J. C.; Cann, K. *Organometallics* **1982**, *1*, 1726.

Table II. The Dependence of the Initial Rate of Consumption of Ethylene on the Formal Concentration of Iron Pentacarbonyl and Temperature Holding Partial Pressures of Carbon Monoxide and Ethylene Constant[a]

T (°C)	$P(CO)_{init}$ (psia)	$P(C_2H_4)_{init}$ (psia)	$[Fe(CO)_5]$ (M)	rate (psi/h)
110	362	118	0.011	4
	355	113	0.011	4
	367	112	0.018	11
	367[b]	122	0.022	13
	369[b]	120	0.022	15
	379	112	0.026	20
	362	122	0.030	36
	364	125	0.030	31
	356	119	0.034	43
	362	119	0.034	43
	368	121	0.037	45
	362	123	0.041	61
120	355	125	0.011	12
	358	121	0.011	13
	358[c]	121	0.011	10
	358	121	0.018	49
	364	121	0.022	71
	352	121	0.030	102
	342	119	0.034	132
130	362	107	0.011	28
140	373	110	0.011	79

[a] Catalyst solution: $Fe(CO)_5$ (variable), KOH (36 mmol), 200 mL (25% H_2O, 75% CH_3OH v/v). Temperature as indicated. [b] Data from Table I. [c] Data shown in Figure 1.

in this case would be $CH_3CH_2C(O)Fe(CO)_3^-$, is attacked by $HFe(CO)_4^-$, in a hydride transfer reaction yielding the product propionaldehyde.

While binuclear iron containing species were first proposed as intermediates for reactions of this nature more than 30 years ago,[7] the lack of spectral evidence for the diiron species most likely to be found under the conditions of these reactions, $HFe_2(CO)_8^-$, suggests that a reaction of the type (ii) is a more likely candidate for the rate-determining step. A hydroformylation mechanism incorporating a bimolecular step of this type is not without precedent. Alemdaroglu, Penninger, and Oltay[21] have invoked just such a step to explain certain features of the analogous hydroformylation reaction catalyzed by cobalt carbonyl hydride, $HCo(CO)_4$, which is of course isoelectronic with $HFe(CO)_4^-$.

A plausible mechanism that incorporates reaction ii above as the rate-determining step is shown in Figure 6. Here the catalytic cycle proper is seen to consist of the addition of ethylene (step 2) to coordinately unsaturated $HFe(CO)_3^-$ which is derived (step 1) from the hydridotetracarbonylferrate ion which is present in abundance in the reaction mixture under the conditions of this reaction. This is followed by hydride migration (step 2′) and CO insertion (step 2″) to produce the coordinately unsaturated iron tetracarbonyl acyl anion, $CH_3CH_2C(O)Fe(CO)_3^-$. As is shown in Figure 6, this latter compound is subject to two reactions; (i) CO addition which yields an unreactive coordinately saturated acylanion (step 4) and (ii) attack by $HFe(CO)_4^-$ (step 3) to produce the product aldehyde, CH_3CH_2CHO, and a diironheptacarbonyl anion which is postulated to undergo (step 5) a series of rapid reactions involving sequential CO addition and hydrolysis to produce $HFe_2(CO)_8^-$ which in turn undergoes thermal decomposition to produce $Fe(CO)_5$ and regenerate $HFe(CO)_3^-$ at the point of entry into this cycle. As shown in Figure 6, the iron pentacarbonyl produced in step 5 is subject to base attack under the conditions of this reaction, thus generating $HFe(CO)_4^-$ according to eq 5. As noted above, step 3 is designated as the rate-determining step of the reaction sequence in order to account for the second-order behavior observed for this reaction with respect to $Fe(CO)_5$ concentration seen in Figure 4.

Step 3 occupies a position of central importance in the scheme shown in Figure 6. This reaction has been studied in detail by Barborak and Cann.[20] They find that $HFe(CO)_4^-$ reacts with $CH_3CH_2Fe(CO)_4^-$ at low temperature to produce propionaldehyde rather than ethane. In their work they clearly demonstrate that the reaction proceeds according to a mechanism involving the addition of $HFe(CO)_4^-$ to the same coordinately unsaturated acyl derivative, $CH_3CH_2C(O)Fe(CO)_3^-$, shown in step 3. They further show that the corresponding coordinately saturated acyl derivative, $CH_3CH_2C(O)Fe(CO)_4^-$, shown as the product of step 4, is unreactive toward $HFe(CO)_4^-$. The completion of the catalytic cycle following step 3 is accomplished by a series of poorly defined CO addition and hydrolysis reactions which terminate in the production of the dinuclear anion $HFe_2(CO)_8^-$. Collmann[19] has shown that in the absence of acid, $HFe_2(CO)_8^-$ undergoes thermal decomposition to produce $HFe(CO)_4^-$ and $Fe(CO)_4$ which can be assumed to revert rapidly to $Fe(CO)_5$ under the high pressures of CO involved in these experiments. More recently, a reaction similar to step 3 has been postulated by Pac and co-workers,[22] who invoke the addition of $HFe(CO)_4^-$ to the coordinately unsaturated hydrido derivative $HFe(CO)_3^-$ as a key step in the generation of H_2 by the photolysis of $HFe(CO)_4^-$ in various mixtures of water and tetrahydrofuran.

There are two additional points to be made concerning the overall characteristics of this reactive system. The first is that, as noted earlier, trace amounts of hydrogen and ethane often accompanied the production of propionaldehyde. The hydrogen production can be attributed to the competing water gas shift reaction which is initiated by the protonation of $HFe(CO)_4^-$ as shown by the side reaction at the top of Figure 6. This reaction is known to proceed quite slowly at the temperatures of these reactions, 110 and 120 °C.[11] The ethane production was likewise found to be quite small and, as indicated previously, the rate of production of C_2H_6 becomes appreciable only at late times in the course of a given reaction. The pH of the reaction mixture was invariably found to have dropped to pH 8.4 or less at these late times, presumably because of the large production of CO_2. The observation by Barborak and Cann that acidification of the saturated alkyl anion $CH_3CH_2Fe(CO)_4^-$ under CO pressure generates ethane[20] suggests that this same reaction (indicated by the lower of the two side reactions shown in Figure 6) is responsible for the ethane production observed at late times in these experiments when the acidity of the reaction mixture has increased to a level sufficient to make this reaction noticeable.

The second and final point of interest concerns the fact that the nature of the base employed in the Reppe hydroformylation plays a major role in determining whether an aldehyde is produced, as in the experiments cited above where KOH is used as the base, or whether the reaction system is sufficiently reducing in nature to cause the aldehyde product to be reduced to the corresponding alcohol as is the case when alkyl amines are used as bases.[1,4,5]

In order to examine this effect more thoroughly, a short series of experiments was carried out in which all variables except base composition were held invariant. Each experiment employed the same 700-mL autoclaves used in the previous experiments and used 200 mL of a 25% H_2O–75% CH_3OH v/v mixture as the solvent to which 4.4 mmol of $Fe(CO)_5$ and 36 mmol of base were added. Initial loading pressures of $P(CO)$ = 300 psig and $P(C_2H_4)$ = 160 psig were used in each experiment. The reaction mixtures were allowed to react for 6 h at 110 °C after which time liquid analyses were performed to determine the relative yields of propionaldehyde and propanol. The analyses, performed with standard gas chromatographic methods with Carbowax-20 as the stationary phase, were greatly simplified by the fact that only the two products of interest, propionaldehyde and propanol, could be identified in the reaction mixture. With pure sodium hydroxide (36 mmol of NaOH), the reaction proceeded rapidly and produced 80 mmol of combined product, 8% of which was 1-propanol, over the 6-h period of reaction. The rate of reaction was somewhat slower when a 50:50 mixture of triethylamine and NaOH (18 mmol of $(C_2H_5)_3N$, 18 mmol of NaOH) was employed and only

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[21] Alemdaroglu, N. H.; Penninger, J. L. M.; Oltay, E. *Monatsh. Chem.* **1976**, *107*, 1153.

[22] Pac, C.; Miyake, K.; Matsuo, T.; Yanagida, S.; Sakuri, H. *J. Chem. Soc., Chem. Commun. 1986*, 1115.

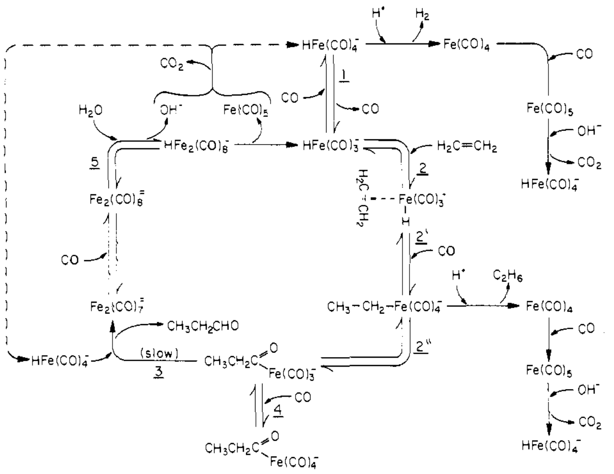


Figure 6. Proposed mechanism for Reppe hydroformylation.

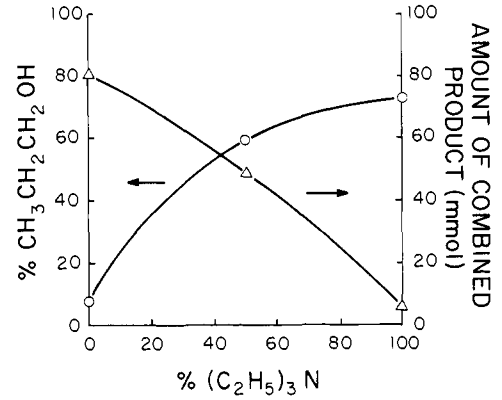
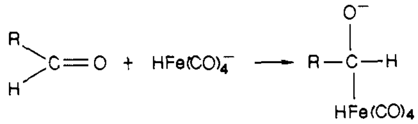
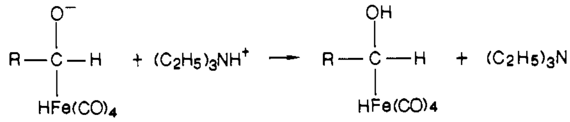


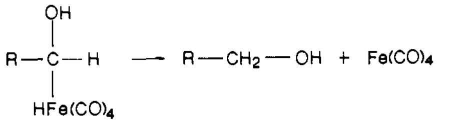
Figure 7. Percentage of product in the form of 1-propanol (○) and overall production after 6 h (△) shown as a function of base composition. Catalyst solution: $Fe(CO)_5$ (4.4 mmol), total base (36 mmol), 200 mL (25% H_2O, 75% CH_3OH v/v). Temperature: 110 °C. Loading pressures at 25 °C: $P(CO) = 300$ psig, $P(C_2H_4) = 160$ psig.

49 mmol of combined product was formed over 6 h. However, the yield of alcohol was greatly enhanced with 1-propanol now constituting 60% of the combined product. The reaction proceeded still more slowly when 100% triethylamine (36 mmol of $(C_2H_5)_3N$) was employed. In this case only 6 mmol of product was formed after 6 h with the product mixture now consisting of 73% 1-propanol and 27% propionaldehyde. These data, shown graphically in Figure 7, clearly illustrate the antithetic changes in alcohol yield and overall rate of reaction that accompany the substitution of triethylamine for sodium hydroxide.

Markö and co-workers[8] have shown that in aqueous solutions triethylammonium hydridotetracarbonylferrate $[(C_2H_5)_3NH]^+[HFe(CO)_4]^-$ rapidly reduces 1-butyraldehyde to 1-butanol while the corresponding sodium salt ($NaHFe(CO)_4$) was unreactive under the same mild conditions. They attribute the reactivity of the trialkylammonium salt to the ease with which the triethylammonium ion can protonate the aldehyde–hydridotetracarbonylferrate adduct in the second step (eq 6b) of the mechanism shown below ($R = C_3H_7$). When $NaHFe(CO)_4$ is used, water or alcohol molecules of the solvent system must serve as proton donors. These are very weak acids compared to $(C_2H_5)_3NH^+$. As a result, the rate of protonation of the aldehyde–hydridotetracarbonylferrate adduct is quite slow. The results shown in Figure 7 are clearly in accord with the observations of Marko' and co-workers. While the volatility of triethylamine may be a factor, the decrease in the rate of the hydroformylation reaction when $(C_2H_5)_3N$ is substituted for NaOH most likely reflects a decrease in the steady-state concentration of $HFe(CO)_4^-$ due to the slower rate of production of $HFe(CO)_4^-$ from the $Fe(CO)_5$ produced by step 5 of the catalytic cycle resulting from the weaker basicity of triethylamine.


$$\mathrm{\overset{R}{\underset{H}{}}C{=}O + HFe(CO)_4^- \longrightarrow R{-}\overset{O^-}{\underset{HFe(CO)_4}{C}}{-}H} \qquad (6a)$$


$$\mathrm{R{-}\overset{O^-}{\underset{HFe(CO)_4}{C}}{-}H + (C_2H_5)_3NH^+ \longrightarrow R{-}\overset{OH}{\underset{HFe(CO)_4}{C}}{-}H + (C_2H_5)_3N} \qquad (6b)$$


$$\mathrm{R{-}\overset{OH}{\underset{HFe(CO)_4}{C}}{-}H \longrightarrow R{-}CH_2{-}OH + Fe(CO)_4} \qquad (6c)$$

$$\mathrm{Fe(CO)_4 + CO \longrightarrow Fe(CO)_5} \qquad (6d)$$

$$\mathrm{Fe(CO)_5 + OH^- \longrightarrow HFe(CO)_4^- + CO_2} \qquad (6e)$$

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Cation- or Solvent-Induced Supermolecular Phthalocyanine Formation: Crown Ether Substituted Phthalocyanines

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Abstract: Phthalocyanines with four 15-crown-5 ether voids at the 3,4-positions (MtCRPc) (Mt = H_2, Zn, Co, Ni, Cu) have been synthesized and characterized. Dimerization of MtCRPc is induced in solvents such as methanol and by addition of some cations (K^+, Ca^{2+}, NH_4^+), especially K^+. Cofacial dimer formation in the presence of these cations proceeds in a two-step three-stage process, as indicated by absorption and emission spectroscopy. These species have a highly specific D_{4h} eclipsed configuration providing well-defined dimeric species for spectroscopic analysis. The ESR spectrum of the cation-induced dimeric CuCRPc shows axial symmetry and may be analyzed in terms of an interplanar separation of 4.1 Å. The ^1H NMR spectra of the cation-induced metal-free and zinc dimers are consistent with an eclipsed configuration. Upper excited state (Soret, S_2) emission is observed for the first time in the phthalocyanine series.

Dimerization, often through aggregation of porphyrins[2] and phthalocyanines,[3] has been intensively investigated. In general the mechanics of aggregation is poorly understood, the product may be contaminated with monomer and perhaps with higher

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