tion of polyion is much less than that of the added electrolyte.

Examination of Tables I and II shows clearly that the effect on γ_{Cl^-} of added 1:2 electrolyte exceeds that expected from just shielding or ionic strength effects. It appears, then, that the Kotin–Nagasawa calculations are applicable to the case of added 1:1 electrolyte and are probably extendable only to the case of a point charge 1:2 electrolyte: for the purposes of this discussion, the principal result of the Kotin–Nagasawa analysis is that f depends only on properties of the polyion. Of course, a polyion model with continuous charge distribution can never display specificity effects. Moreover, the results of our experiments clearly indicate that the structure of the counterion is also of importance, and the Kotin–Nagasawa theory cannot deal

with such specific features of ionic structure. However, to the extent that it is valid to identify the minimum in the counterion distribution function (with distance away from the polyion) with the boundary between free and associated counterions, and to the extent that it is valid to use the Bjerrum approximation of relating the densities of associated and free ions in terms of an equilibrium constant, the discussion of γ_{Cl^-} given above is useful. Examination of the data and the arguments used then further reinforces the observation that specific interactions may exist between counterion and polyion and may be of importance in determining the counterion distribution.

IV. Acknowledgments.—We wish to thank the United States Public Health Service for financial support.

Hydrogenation under Hydroformylation Conditions: Observations, Kinetics, and Mechanism

BY CLYDE L. ALDRIDGE[1] AND HANS B. JONASSEN

Reduction of aldehyde to alcohol under hydroformylation conditions (cobalt catalyst, 160°, hydrogen and carbon monoxide pressures) appears to comprise a two step sequence (a) a heterogeneous hydrogenolysis in which dicobalt octacarbonyl is cleaved to yield cobalt hydrocarbonyl and for which metallic cobalt is the catalyst, followed by (b) a homogeneous hydrogen exchange in which cobalt hydrocarbonyl acts as a reducing agent for the aldehyde. Thiophene and traces of moisture act as poisons. These effects, together with residual surface effects of lead compounds and the concentration dependence of poisoning by lead compounds, are consistent with metallic cobalt catalysis of the hydrogenolysis. The kinetic dependence of the unpoisoned reaction on the variables was determined and a mechanism for the homogeneous hydrogen transfer is proposed.

Introduction

During hydroformylation of an olefin in the presence of a cobalt-containing catalyst some reduction of aldehyde to alcohol and even of the olefin to paraffin occurs, and at temperatures approaching 200° these reductions become major reactions.[2–5] The homogeneous aspects of this reduction of aldehyde have been emphasized in the literature[2–4,6,7] and the reaction interpreted as occurring by a homogeneous free radical chain,[2] by an ionic addition of cobalt hydrocarbonyl to the aldehyde and abstraction of a hydrogen from another molecule of cobalt hydrocarbonyl[6] and by a homogeneous reaction of molecular hydrogen with an aldehyde-cobalt hydrotricarbonyl adduct.[7]

The evidence for homogeneous catalysis of this reaction consists of two experiments: (a) reduction of aldehyde in a hydroformylation reaction mixture still occurs in the presence of certain sulfur-containing compounds, e.g., thiophene,[2–4] and (b) reduced cobalt catalyzes reduction of aldehyde when no carbon monoxide is present, fails to do so when a small amount of carbon monoxide is in the system and regains its activity at higher carbon monoxide pressures.[3]

Recently we have reported that this reaction has a heterogeneous character in that it is subject to poisoning by heavy metal ions which are reducible to the *metal* by the metallic cobalt present in the system and we

have pointed out that consideration must be given to the dynamic equilibrium between cobalt metal and cobalt carbonyls.[8]

This paper reports the results of experiments designed to answer the following questions concerning reduction of aldehyde under hydroformylation conditions. (1) Is a free radical process occurring in this system? (2) Is this catalysis subject to partial poisoning by a sulfur compound, such as thiophene, to a degree that is consistent with a metallic catalyst that is constantly being regenerated? (3) What are the precise kinetic dependences of this reaction on the concentration of the several components—H_2, CO, aldehyde, and cobalt—and can a mechanism be deduced therefrom which is consistent with these and other experimental facts? (4) What is the mode of poisoning by heavy metals and other poisons?

Discussion

Evidence against a Free Radical Process.—Because of the extremely low energy of the carbonyl–hydrogen bond (<78 kcal./mole),[9] the easiest reaction an aldehyde can undergo with a free radical is loss of this hydrogen atom to yield an acyl radical. With branched aldehydes this radical readily loses carbon monoxide to give large yields of the corresponding paraffin.[10,11]

It was demonstrated that 2-ethylhexanal when treated under hydroformylation temperature and pressure conditions with di-t-butyl peroxide (6.5 mole %) yielded the decarbonylation product, n-heptane (30 mole %) (Table I). However, when this aldehyde was reduced under these temperature and pressure conditions *via* cobalt carbonyl catalysis no n-heptane was

(1) Esso Research Laboratories, P. O. Box 551, Baton Rouge, Louisiana. Robert A. Welch Visiting Scholar to A. and M. College of Texas, 1961-1962.

(2) I. Wender, R. Levine and M. Orchin, *J. Am. Chem. Soc.*, **72**, 4375 (1950).

(3) I. Wender, M. Orchin and H. H. Storch, *ibid.*, **72**, 4842 (1950).

(4) H. Adkins and G. Krsek, *ibid.*, **71**, 3051 (1949).

(5) Fiat, Final Report 1000, "The Oxo Process," issued by the Office of Military Government for Germany through the Office of Technical Service of the U. S. Department of Commerce, PB81383, p. 26.

(6) M. Orchin, "Advances in Catalysis," Vol. 5, Academic Press, New York, N. Y., 1953, pp. 385-415.

(7) L. Marko, *Proc. Chem. Soc.*, 67 (1962).

(8) C. L. Aldridge and H. B. Jonassen, *Nature*, **188**, 404 (1960).

(9) T. L. Cottrell, "The Strengths of Chemical Bonds," Academic Press, New York, N. Y., 1954, p. 190.

(10) P. Thuring and A. Perrett, *Helv. Chim. Acta*, **36**, 13 (1953).

(11) F. H. Seubold, Jr., *J. Am. Chem. Soc.*, **76**, 3732 (1954).

TABLE I

DECARBONYLATION OF 2-ETHYLHEXANAL[a]

$Co_2(CO)_8$,[b] mmole/l.	0	6.30
Di-t-butyl peroxide, mmole/l.	20.6	0
Aldehyde conversion, mole %	..	75[c]
n-Heptane yield, mole %	30.2	0.00

[a] 2-Ethylhexanal (314 mmoles/l.) in di-n-hexyl ether, 160°, 310 min. reaction time, 925 p.s.i. carbon monoxide and 725 p.s.i. hydrogen partial pressures. [b] Amount originally charged. [c] Includes by-product 2-ethylhexyl formate as well as 2-ethylhexanol.

formed (Table I). It was demonstrated that 0.01 mole % yield of n-heptane would have been detected by the gas chromatographic analysis used. The possibility of a free radical mechanism was further tested by determining the effect of di-t-butyl peroxide and of hydroquinone on the rate of reduction of aldehyde to alcohol. Reduction of 2-ethylhexanal to 2-ethylhexanol (excluding conversion to formate ester) in di-n-hexyl ether solution first was shown not to deviate from first order dependence on aldehyde concentration to at least 75% conversion. The apparent first order rate constant, k, was determined in the first 40% of a reaction; hydroquinone (91.5 mole % on dicobalt octacarbonyl catalyst charged, 1.83 mole % on aldehyde) was then injected and k determined in the succeeding portion of the reaction. A similar comparison was made with di-t-butyl peroxide (50 mole % on dicobalt octacarbonyl charged, 1% on aldehyde). No effect on the rate constant was observed in either case (Table II). These results indicate that aldehyde reduction does not proceed via a free radical mechanism and that other free radicals do not exist in appreciable quantity in this system.

TABLE II

EFFECT OF FREE RADICAL SOURCE AND ACCEPTOR ON RATE[a]

Additive		k, after additive injected[b]
Name	mmole/l.	k, before additive injected
Di-t-butyl peroxide	3.17	1.02
Hydroquinone	5.80	0.99

[a] 2-Ethylhexanal (314 mmoles/l.) in di-n-hexyl ether, 160°, 950 p.s.i. CO and 800 p.s.i. hydrogen partial pressures, 6.30 mmoles/l. dicobalt octacarbonyl charged. [b] k = apparent first order aldehyde reduction rate constant for these conditions.

Effect of Thiophene and Traces of Water.—A careful comparison of first order reaction rate constants before and after injection of thiophene demonstrated that this material poisons the reaction to a substantial degree (Table III). At 160° and 950 p.s.i. carbon monoxide and 750 p.s.i. hydrogen partial pressures the maximum effect on the rate was 25%. If thiophene were competing kinetically with the aldehyde for the cobalt hydrocarbonyl an apparent poisoning effect might occur, but it would seem that additional incremental quantities of thiophene should continue to have an effect. Much greater effects were observed at higher temperatures (69% poisoning at 185°) and at lower carbon monoxide pressures (42% poisoning at 658 p.s.i. of carbon monoxide) where the cobalt carbonyls are less stable. If thiophene were poisoning by complexing with a carbon monoxide deficient species, e.g., cobalt hydrotricarbonyl, then just the opposite effect of conditions should be observed, i.e., under conditions where more carbon monoxide deficient species would be present the thiophene should be less effective. Quantitative comparisons with these more severe conditions may however contain some error because under these more severe conditions the thiophene also promoted the deposition of a cobalt mirror on the walls of the reactor. The thiophene apparently slowed the consumption of metallic cobalt by the carbon

monoxide and thus promoted the deposition of a relatively thick mirror. Thiophene is difficult to hydrogenate by metallic catalysts[12] and under none of these conditions was any reaction or loss of thiophene detected. These effects of thiophene are consistent with a poisoning of metallic cobalt which is constantly being consumed and regenerated.[3]

TABLE III

POISONING OF ALDEHYDE REDUCTION TO ALCOHOL BY THIOPHENE AND BY WATER[a]

Poison		k, with poison[b]
Name	mmole/l.	k, without poison
Thiophene	9.5[c]	0.96
Thiophene	31.6[c]	.86
Thiophene	94.9[c]	.75
Thiophene	316[c]	.75
Water	1.5[d]	.89
Water	9.3[d]	.88
Water	18.9[e]	.89
Water	369[f]	.88

[a] 2-Ethylhexanal (316 mmoles/l.) in di-n-hexyl ether, 160°, 750 p.s.i. of hydrogen and 950 p.s.i. of carbon monoxide partial pressures, 6.30 mmoles/l. of dicobalt octacarbonyl charged. [b] k = apparent first order aldehyde reduction rate constant for these conditions. [c] Dissolved in di-n-hexyl ether and injected into autoclave in middle of reaction. [d] Dissolved in diethyl ether and injected in middle of reaction. [e] Charged initially with the di-n-hexyl ether. [f] Injected without solvent in middle of reaction.

During the course of this work a small drift of reaction rate constants was observed due to seasonal changes in atmospheric relative humidity. Thus water in trace quantities is also a poison (Table III). The addition of 9.5 mg. of water to a 1-liter autoclave had as much effect as 2.3 g. The behavior of a rigorously anhydrous reaction would be most interesting together with determination of poisoning vs. water concentration at very low concentrations. Since moisture on a surface inhibits the decomposition of cobalt hydrocarbonyl,[13] it seems reasonable that moisture should also inhibit the formation of cobalt hydrocarbonyl on a surface. This then appears to be the effect which is observed here with water and with thiophene. To confirm this the amount of cobalt hydrocarbonyl in the liquid phase during reduction of an aldehyde was determined both in the absence and in the presence of thiophene (95 mmoles/l.). In the former case the cobalt hydrocarbonyl in the liquid phase (there is some in the gas phase, see below) amounted to 56% of the dicobalt octacarbonyl originally charged and in the latter case 43%. This decrease is of the same order as the degree of poisoning of aldehyde reduction. Thus, these poisons appear to slow the formation and decomposition of cobalt hydrocarbonyl so that when it is consumed by a competing process (reduction) its concentration is diminished. Interestingly enough, carbon monoxide also inhibits the reaction of hydrogen with dicobalt octacarbonyl to form cobalt hydrocarbonyl at room temperature.[14]

Heavy Metal Poisons.—Recently we reported that ions of the heavy metals lead, mercury and bismuth are poisons for hydrogenation of aldehyde under hydroformylation conditions.[8] These ions have oxidation–reduction potentials such that they are reducible by metallic cobalt (present in the system[15,16])
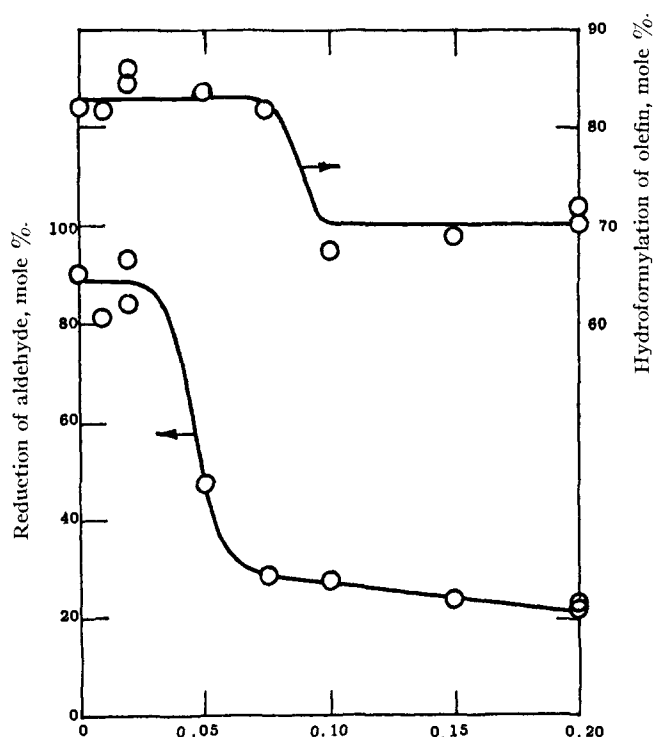
(12) H. D. Hartough, "Thiophene and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1952, p. 167.

(13) W. Hieber and J. Sedlmeier, Angew. Chem., 65, 534 (1953).

(14) P. Pino, R. Ercoli and F. Calderazzo, La Chimica E. L'Industria, 37, 782 (1955).

(15) H. W. Sternberg, I. Wender and M. Orchin, Anal. Chem., 24, 174 (1952).

(16) See Ref. 5, p. 12.

G. atom of lead per g. atom of total cobalt in the reaction mixture

Fig. 1.—Effect of lead distearate on hydroformylation of olefin and on hydrogenation of aldehyde. Conditions same as listed under Table IV.

to the corresponding metals. Conversely thallic ion which is not reducible to the metal has no effect. Additional experiments under these conditions revealed that lead distearate not only affects the degree of hydrogenation of aldehyde in the experiments to which it is added, but it also had a residual effect on the succeeding run (Table IV); even though the autoclave was thoroughly cleaned both mechanically and with organic solvents between experiments. Undoubtedly this residual effect comes from an alteration of the character of the autoclave surface.

TABLE IV
RESIDUAL EFFECT OF LEAD ON SUCCESSIVE HYDROFORMYLATION EXPERIMENTS[a]

Expt.	Pb(stearate)₂, mmole/l.	Hydroformylation of olefin, mole %	Reduction of aldehyde, mole %
1	None	82	90
2	4	70	22
3	None	81	33
4	None	83	92
5	3	69	24
6	None	82	33
7	None	81	83

[a] Heptenes, cobalt (0.020 g. atom/l.) charged as cobaltous oleate, 177°, 3000 p.s.i. pressure, hydrogen partial pressure decreased from 1750 p.s.i. to as low as 1230 p.s.i. depending on the amount of hydrogenation which occurred in the given reaction, 6 hr.

Further experiments with varying amounts of lead revealed an interesting dependence on concentration of the poison. At less than about 0.02 g. atom of lead per g. atom of cobalt little if any poisoning is observed. Between 0.02 and 0.06 g. atom/g. atom a sharp degree of poisoning develops and above 0.06 little additional effect occurs (Fig. 1). The shape of this curve and the small amount of lead needed for its principal effect eliminates the stoichiometric removal of cobalt hydrocarbonyl (via, e.g., stable salt formation) as the cause of poisoning. Instead the shape of the
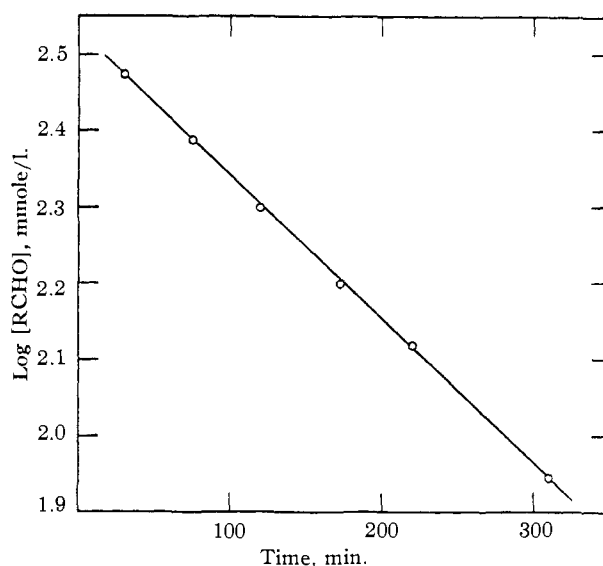

Fig. 2.—First order dependence of reaction on aldehyde concentration: 160°, 915 p.s.i. CO and 765 p.s.i. H₂ partial pressures, 316 mmoles/l. 2-ethylhexanal in di-n-hexyl ether, 2-ethylhexanol to 2-ethylhexyl formate product ratio remained 76/24 throughout experiment.

curve is that observed in the poisoning of solid metallic catalysts, e.g., nickel and palladium, by alloying with them the heavy metals, e.g., lead, bismuth, copper and gold.[17-21] The greater effect on conversion of aldehyde to alcohol than of olefin to hydroformylation product in these experiments is understandable in view of these facts: (a) these are successive reactions and (b) the hydrogenation is a relatively slow reaction. Identical poisoning effects on the hydroformylation and the hydrogenation rate constants would produce for a given over-all time of reaction such divergent percentage conversions for the two reactions as shown in Fig. 1.

After an aldehyde hydrogenation under conditions for especially rapid reaction, the surface of the autoclave has an iridescent blue-purple tint or at times a dull black color, either of which is removable by wiping, and which does not constitute a significant weight of cobalt. While the experiments on residual effects of lead indicate an importance of the condition of autoclave surface they do not eliminate the possibility that some microscopic (or atomic) particles of cobalt are dispersed in the medium as well. Such highly dispersed chromium, cobalt and nickel have been observed in reactions of certain organometallic compounds.[22]

Dehydrogenation.—During the course of the kinetic study described below an experiment was conducted in which no hydrogen was added. The C.P. carbon monoxide (maximum impurities specified as 0.5%) contained by mass spectroscopic and gas chromatographic analyses 0.3% hydrogen which under the conditions of 160° and 990 p.s.i. amounted to 3 p.s.i. of hydrogen pressure. After seven hours the aldehyde had absorbed 4.6 p.s.i. of hydrogen as determined by conversion to alcohol. The effluent gas from this reaction contained 1.1% hydrogen or 11 p.s.i. hydrogen under reaction conditions. Inasmuch as other hydrogen producing processes, e.g., dehydrogenation of the aldehyde to give 2-ethylhexenal did not occur, dehydrogenation of the di-n-hexyl ether solvent apparently

(17) D. A. Dowden and P. W. Reynolds, Discussions Faraday Soc., 8, 184 (1950).
(18) A. Couper and D. D. Eley, ibid., 8, 172 (1950).
(19) P. W. Reynolds, J. Chem. Soc., 265 (1950).
(20) H. Lindar, Helv. Chim. Acta, 35, 446 (1952).
(21) C. Paal and A. Karl, Ber., 46, 3069 (1913).
(22) H. Zeiss, "Advances in the Chemistry of the Coördination Compounds," S. Kirschner, editor, The Macmillan Co., New York, N. Y., 1961, p. 88.
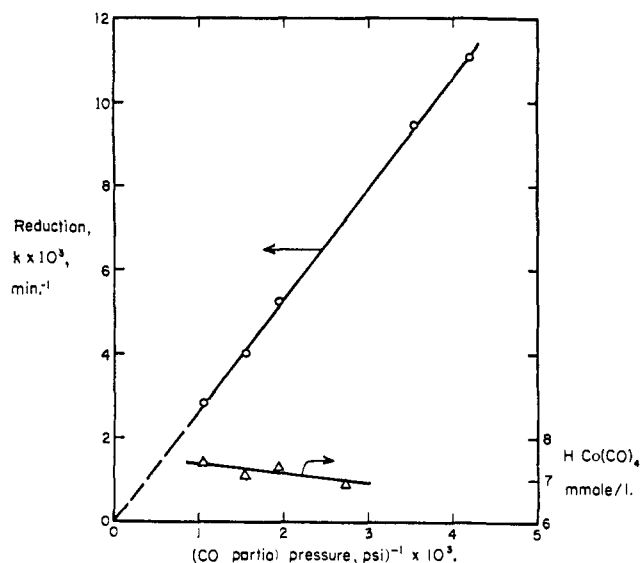
Fig. 3.—Effect of carbon monoxide on rate of aldehyde reduction and on cobalt hydrocarbonyl concentration: 316 mmoles/l. 2-ethylhexanal in di-n-hexyl ether, 160.0°, 770 p.s.i. H_2 partial pressure, 6.30 mmoles of $Co_2(CO)_8$ charged per l.

was the source of this hydrogen. This dehydrogenation may lend support to the evidence for metallic cobalt as the active hydrogenation catalyst in this system. Further study of this aspect is being planned.

Kinetic Study of the Unpoisoned Reaction.—A kinetic study of the effect of hydrogen and carbon monoxide partial pressures and cobalt concentration on reduction of aldehyde to alcohol was made under non-poisoning conditions. By-product formate ester was determined separately and its formation is not included in this study. 2-Ethylhexanal was used for this study because of its low vapor pressure and its ready availability and most importantly because its α branch prevents condensation reactions, e.g., aldolization, which could obscure the results.

The conversion of aldehyde to alcohol is first order in aldehyde concentration (Fig. 2). In the range of 239 to 953 p.s.i. of carbon monoxide at 160°, the apparent first order reaction rate constant, k, is found to be inversely proportional to the first power of the carbon monoxide pressure (Fig. 3). Extrapolation of the curve to infinite carbon monoxide pressure gives an intercept at $k = 0$, showing that at high carbon monoxide pressure no hydrogenation will occur. This inverse dependence on carbon monoxide pressure is similar to that reported for hydroformylation of olefin.[23] Dependence on the reciprocal first power of the carbon monoxide pressure is in disagreement though with a recent report of work at a higher but overlapping pressure range.[7] The concentration of cobalt hydrocarbonyl in the liquid phase was determined[15] in these experiments; its concentration *per se* bears no relationship to the rate of aldehyde reduction (Fig. 3).

At low hydrogen partial pressures, i.e., up to about 100 p.s.i., the rate is dependent on the one-half power of hydrogen pressure; as hydrogen pressure is further increased a progressive decrease in dependence is observed. In the increment from 368 to 760 p.s.i. the apparent rate constant increases only as the 0.13 power of hydrogen (Fig. 4). This variable dependence on hydrogen can be calculated by considering the catalyst equilibria involved (described below).

The dependence of rate on the concentration of dicobalt octacarbonyl charged to the reaction likewise is fractional. In the range of 6.30 to 25.2 mmoles/l. of
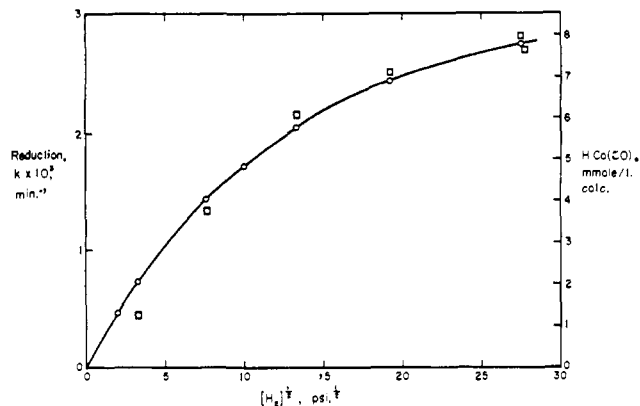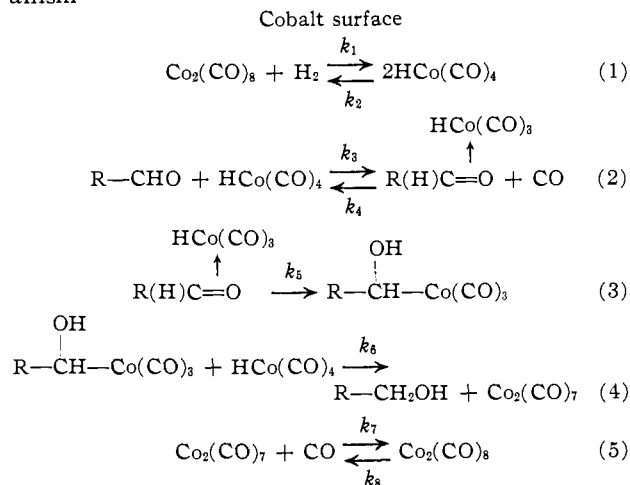
(23) G. Natta, R. Ercoli, S. Castellano and F. H. Barbieri, *J. Am. Chem. Soc.*, **76**, 4049 (1954).

Fig. 4.—Effect of H_2 pressure on reduction of aldehyde and on concentration of $HCo(CO)_4$: O $HCo(CO)_4$, mmole/l., calculated from Eq. 11; □ experimental (apparent) aldehyde reduction rate constants, $k \times 10^3$ min.$^{-1}$. Conditions: 160.0°, 955 p.s.i. CO partial pressure, 316 mmoles/l. 2-ethylhexanal in di-n-hexyl ether, 6.30 mmole/l. $Co_2(CO)_8$ charged.

dicobalt octacarbonyl the dependence is about 0.8 order. This value also can be calculated from the catalyst equilibria.

These kinetic dependences as well as the effects of poisons on this reaction can be explained by the mechanism

$$\text{Cobalt surface}$$

$$Co_2(CO)_8 + H_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} 2HCo(CO)_4 \qquad (1)$$

$$HCo(CO)_3$$
$$\uparrow$$
$$R\text{—CHO} + HCo(CO)_4 \underset{k_4}{\overset{k_3}{\rightleftarrows}} R(H)C\text{==}O + CO \qquad (2)$$

$$HCo(CO)_3 \qquad\qquad OH$$
$$\uparrow \qquad\qquad\qquad |$$
$$R(H)C\text{==}O \xrightarrow{k_5} R\text{—CH—}Co(CO)_3 \qquad (3)$$

$$OH$$
$$|$$
$$R\text{—CH—}Co(CO)_3 + HCo(CO)_4 \xrightarrow{k_6}$$
$$\qquad\qquad\qquad\qquad R\text{—CH}_2OH + Co_2(CO)_7 \qquad (4)$$

$$Co_2(CO)_7 + CO \underset{k_8}{\overset{k_7}{\rightleftarrows}} Co_2(CO)_8 \qquad (5)$$

From equations 2, 3 and 4, assuming that in a non-poisoned condition the catalyst equilibria (eq. 1 and 5) are satisfied and hence the individual steps, i.e., k_1, k_2, k_7 and k_8, are not rate limiting, the rate equation becomes

$$\frac{d[RCH_2OH]}{dt} = \frac{k_3[RCHO][HCo(CO)_4]}{\frac{k_4}{k_5}[CO] + 1} \qquad (6)$$

For $k_4 \gg k_5$, i.e., k_5 fully rate limiting, then the 1 becomes negligible and

$$\frac{d[RCH_2OH]}{dt} = \frac{k_3k_5[RCHO][HCo(CO)_4]}{k_4[CO]} \qquad (7)$$

Ignoring the small amount of metallic cobalt which is formed, the dicobalt octacarbonyl originally charged to the reactor, C_x, distributes itself between dicobalt octacarbonyl in the liquid phase and cobalt hydrocarbonyl (eq. 1). The cobalt hydrocarbonyl is partitioned between liquid and gas phases

$$K_x = \frac{[HCo(CO)_4]\ \text{moles in liquid phase}}{[HCo(CO)_4]\ \text{moles in gas phase}} = 2.8 \qquad (8)$$

K_x was determined experimentally for the solvent and amount of liquid charge used in this work to be 2.8. Thus stoichiometrically

$$C_x = Co_2(CO)_8 + \tfrac{1}{2}[HCo(CO)_4]\text{gas} + \tfrac{1}{2}[HCo(CO)_4]\text{liq.} \qquad (9)$$

from eq. 1

$$K_y = \frac{k_1}{k_2} = \frac{[HCo(CO)_4]^2}{[Co_2(CO)_8][H_2]} \qquad (10)$$

Solving equations 8, 9, and 10 we obtain

$$[HCo(CO)_4] =$$
$$K_y^{1/2}[H_2]^{1/2}\sqrt{C_x + 0.11526\,K_y[H_2]} - 0.3395K_y[H_2] \quad (11)$$

Thus the full rate equation becomes

$$\frac{d[RCH_2OH]}{dt} =$$
$$\frac{k_3k_5[RCHO]\{K_y^{1/2}[H_2]^{1/2}(C_x+0.11526K_y[H_2])^{1/2}-0.3395K_y[H_2]\}}{k_4[CO]}$$
$$(12)$$

It thus is apparent why the rate is proportional to $[H_2]^{1/2}$ at low hydrogen partial pressures and becomes less dependent at higher hydrogen partial pressures. K_y (dicobalt octacarbonyl and cobalt hydrocarbonyl are expressed in moles per liter and hydrogen partial pressure in pounds per sq. in.) was determined experimentally to be approximately 8×10^{-5} under these conditions. This value of K_y is in general agreement with the value which can be calculated from data previously reported for somewhat different conditions.[24] Using this value of K_y, $HCo(CO)_4$ concentrations are calculated from eq. 11 at various hydrogen partial pressures and compared in Fig. 4 with observed apparent rate constants, k, of aldehyde conversion to alcohol.
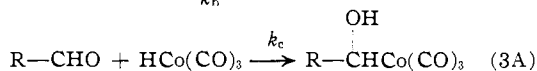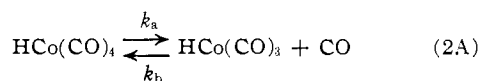
The fractional catalyst dependence arises from these catalyst equilibria as well. The calculated (eq. 11) and experimental values for order with respect to dicobalt octacarbonyl charged, C_x, are compared in Table V.

TABLE V

DEPENDENCE OF ALDEHYDE REDUCTION ON
CATALYST CONCENTRATION[a]

| C_x,[b] | Order of reaction with respect to C_x | |
mmole/l.	Experimental	Calculated[c]
6.30		
	0.7	0.8
12.6		
	0.8	0.8
25.2		

[a] 2-Ethylhexanal (316 mmoles/l.) in di-n-hexyl ether, 160°, 768 p.s.i. H_2 and 955 p.s.i. CO partial pressures. [b] $Co_2(CO)_8$ concentration originally charged. [c] Calculated from eq. 11 as applied to eq. 12.

The mode of carbon monoxide loss and addition to aldehyde by cobalt hydrocarbonyl may differ somewhat in detail from that depicted in eq. 2 and 3 without altering the rate equation; e.g., we may assume that carbon monoxide loss precedes addition to aldehyde thus postulating, as has been done for hydroformylation of olefin,[25] cobalt hydrotricarbonyl as a discrete intermediate (eq. 2A and 3A below).

$$HCo(CO)_4 \underset{k_b}{\overset{k_a}{\rightleftarrows}} HCo(CO)_3 + CO \qquad (2A)$$

$$\overset{\qquad\qquad OH}{R\text{—}CHO + HCo(CO)_3 \overset{k_c}{\longrightarrow} R\text{—}\overset{|}{C}HCo(CO)_3} \quad (3A)$$

In this case the rate equation becomes

$$\frac{d[RCH_2OH]}{dt} = \frac{k_a[RCHO][HCo(CO)_4]}{\frac{k_b}{k_c}[CO] + [RCHO]} \qquad (13)$$

or when $k_b \gg k_c$, i.e., equilibrium of eq. 2A undisturbed

$$\frac{d[RCH_2OH]}{dt} = \frac{k_ak_c[RCHO][HCo(CO)_4]}{k_b[CO]} \qquad (14)$$

(24) M. Orchin, L. Kirch and I. Goldfarb, J. Am. Chem. Soc., 78, 5450 (1956).

(25) R. F. Heck and D. S. Breslow, ibid., 83, 4023 (1961).

Conclusion as to Mechanism.—On the basis of these several reaction characteristics it appears that reduction of aldehyde under hydroformylation conditions must be thought of as comprising two major parts—first, the in situ formation of an inorganic reducing agent, cobalt hydrocarbonyl, by a hydrogenolysis reaction which is probably heterogeneous, involving metallic cobalt as the catalyst; and second, the reduction of aldehyde by this inorganic reducing agent, which reduction is homogeneous.

Experimental

Apparatus.—Aldehyde reduction reactions were carried out in a one liter stainless steel stirred autoclave. A thermistor and relay actuated a coolant pump which maintained the desired temperature. A liquid injection manifold allowed the injection of materials as desired under experimental conditions. A sample line and cooling coil with total holdup of <1 ml. allowed the withdrawal of representative small samples without appreciably upsetting the system.

Materials.—2-Ethylhexanal and di-n-hexyl ether were Eastman White Label. Lead distearate was Witco Chemical Co. grade 30. Matheson prepurified hydrogen and C.P. carbon monoxide were used. Other materials were the highest purity available commercially.

Analytical Methods.—Analyses of products from the 2-ethylhexanal experiments were by gas chromatography. Analyses of products from hydroformylation of C_7 olefin were by distillation, infrared spectra and chemical functional group analyses.[26,27] Cobalt hydrocarbonyl was determined by precipitation with o-phenanthroline-nickelous chloride solution and volumetric analysis of the CO.[15] Samples for this analysis were taken through the cooling coil at such a speed that the time before cooling to near room temperature was of the order of 0.02 sec. From the cooling coil the sample passed directly into the precipitating reagent.

Catalyst Preparation.—A dispersion of cobaltic oxide (8.860 g.) in di-n-hexyl ether (406 ml.) was allowed to react in a one liter autoclave with 1350 p.s.i. of carbon monoxide and 600 p.s.i. of hydrogen pressures at 160° until absorption of gas ceased (1.25 hr.). The autoclave was cooled to room temperature, vented to atmospheric pressure, flushed with 150 p.s.i. of carbon monoxide, and pressured to 150 p.s.i. with carbon monoxide. It was then allowed to stand overnight to let water formed settle out and cobalt hydrocarbonyl be converted to dicobalt octacarbonyl. Analysis of the solution[15] showed it to contain 0.130 mmole of dicobalt octacarbonyl per ml.

2-Ethylhexanal Reductions.—Prior to each experiment the autoclave was cleaned by stirring for one hour at 160° with 500 ml. of methanol and 800 p.s.i. carbon monoxide pressure followed by wiping with clean cloths and standing open overnight. Typically, 275 ml. of di-n-hexyl ether was charged to the one liter autoclave and the system flushed four times with 100 p.s.i. of carbon monoxide. It was then pressured to 100 p.s.i. with carbon monoxide and heated to the desired temperature. After pressuring to the desired carbon monoxide pressure and allowing the temperature to become stabilized the desired amount of catalyst solution (diluted to 27.5 ml. with di-n-hexyl ether) was injected into the autoclave with hydrogen to within 150 p.s.i. of the desired total pressure. The catalyst was allowed to equilibrate one hour under these conditions whereupon the aldehyde, diluted to 44.5 ml., was injected with the remainder of the hydrogen. Samples were periodically taken. After the apparent first order reaction rate constant, k, was established (i.e., by the time ca. 40% of the aldehyde was converted) thiophene dissolved in 15 ml. of di-n-hexyl ether was injected with hydrogen to the original pressure and k again determined.

For reactions at low hydrogen pressure where greater precision was required the catalyst and aldehyde were injected with carbon monoxide and the hydrogen pressure added last.

Reproducibility of this procedure was found during periods of stable relative humidity to be better than $\pm 2\%$.

Water was added in three different ways: at the beginning when charging the autoclave, in the middle of the experiment as described above except dissolved in 25 ml. of diethyl ether and in the case of the larger amounts injection without solvent.

In all experiments corrections for thermal expansion, carbon monoxide compression (due to liquid injection and sample withdrawal) and solubility effects were made and average pressures calculated. Temperatures were controlled at the indicated levels within 0.1° with fluctuations of <0.2° around the mean.

Products from appropriate experiments were separated by distillation, purified by gas chromatography and identified as follows: n-Heptane: gas chromatographic retention time and

(26) S. Siggia, "Quantitative Organic Analysis via Functional Groups," 2nd Ed., J. Wiley and Sons, New York, N. Y., 1954, pp. 8–13.

(27) D. M. Smith and J. Mitchell, Jr., Anal. Chem., 22, 750 (1950).

infrared spectrum identical with an authentic sample, $n^{30.6}$D 1.3826 (authentic sample $n^{30.6}$D 1.3828). *2-Ethylhexanol:* retention time and infrared spectrum identical with an authentic sample, $n^{29.6}$D 1.4271 (authentic sample $n^{29.6}$D 1.4281). *2-Ethylhexyl formate:* infrared spectrum characteristic of formate ester (strong peaks at 8.48 and 5.78 μ), $n^{29.6}$D 1.4168, *Anal.* Calcd. for $C_9H_{18}O_2$: C, 68.31; H, 11.47. Found: C, 68.53, 68.65; H, 11.33, 11.60.

Cobalt Distribution and Determination of K_x.—2-Ethylhexanal (316 mmoles per l. in dihexyl ether) was reduced according to the above described general procedure at 160°, 754 p.s.i. hydrogen partial pressure, 950 p.s.i. carbon monoxide partial pressure and 6.30 mmoles per liter of dicobalt octacarbonyl charged (C_x). When the reduction of aldehyde was 50% complete a liquid aliquot (by wt.) was taken through the cooling coil, at such a rate that the time before cooling to approximately room temperature was approximately 0.02 sec. The depressured and cooled sample was directed into a solution of nickelous chloride–*o*-phenanthroline complex and analyzed for cobalt hydrocarbonyl.[15] Another aliquot (by wt.) was similarly withdrawn, collected in a suitable glass container, and analyzed for total cobalt carbonyls gasometrically.[15] The liquid reaction medium contained 59% of the original cobalt as cobalt hydrocarbonyl and 21% as dicobalt octacarbonyl. Two reactions under conditions identical with the above were conducted in which 15% aliquots of the gas were passed rapidly (5,000 ml./min.) through the cooling coil to a sintered glass filter stick immersed in nickelous chloride–*o*-phenanthroline solution. The precipitate which formed in solution and on the sintered glass was collected and analyzed gasometrically.[15] The gas phase in the autoclave was thus found to contain 24% of the originally charged cobalt as cobalt hydrocarbonyl; over-all cobalt balance, 104%. On cooling, depressuring, and opening the autoclave, a slight color of metallic cobalt was observed on the internal surfaces which were below the liquid level; the amount was too small to be physically recoverable although the color was easily removable by wiping.

The analyses of the liquid samples are believed to be the more accurate; for calculation of K_x the cobalt hydrocarbonyl in the gas phase was taken as the difference between dicobalt octacarbonyl charged and the total cobalt carbonyls in the liquid phase. Four such determinations in separate experiments gave an average value of K_x of 2.8; σ, 0.15.

Determination of K_y.—In experiments at 160° to which no poison was added and which included 4 levels of hydrogen partial pressures from 11 to 770 p.s.i., 3 levels of catalyst concentrations (C_x) from 6.30 to 25.2 mmoles/l., 3 levels of carbon monoxide partial pressures from 500 to 960 p.s.i., and 2 levels of 2-ethylhexanal concentrations 78.5 and 316 mmoles/liter, liquid samples were taken as described above at about 50% completion of aldehyde reduction and analyzed[15] gasometrically for total cobalt carbonyl and cobalt hydrocarbonyl. Concentrations of dicobalt octacarbonyl and cobalt hydrocarbonyl were determined and corrected for thermal expansion of the organic medium on reactor conditions. K_y then was calculated from equation 10 with dicobalt octacarbonyl and cobalt hydrocarbonyl concentrations expressed in moles per liter and hydrogen partial pressure in pounds per sq. in. Eight determinations gave an average value of 8×10^{-5}; σ 1.8×10^{-5}.

Hydroformylation of Heptenes.—Prior to an experiment all internal surfaces of the three-liter autoclave were cleaned with steel wool and hydrocarbon solvent and polished with clean white cloths. One liter of heptenes prepared by copolymerization of propene and butene[28] together with the tabulated quantities of cobaltous oleate and other metal soap was then charged to the autoclave. The free space was flushed with synthesis gas by pressuring twice to approximately 500 p.s.i. and carefully venting. The autoclave was pressure tested at 3000 p.s.i. and then slowly vented to 1500 p.s.i. The autoclave was heated with shaking to 177° over a period of about 1.5 hours. When the reaction started, as evidenced by a sharp drop in pressure, the pressure was raised to 3000 p.s.i. Each time the pressure dropped to 2500 p.s.i. it was raised back to 3000 p.s.i. The first two or three such pressure drops were very rapid and were accompanied by a momentary rise of several degrees in temperature. In these cases the temperature was allowed to subside to 177° before additional gas was added, whereupon the pressure would drop to as low as 1000 p.s.i. The hydroformylations were continued for a total of six hours after the first pressure drop. The autoclave was then cooled to room temperature with an external flow of air. The autoclave was flushed twice with 500 p.s.i. of hydrogen and then pressured to 150 p.s.i. with hydrogen. To decompose the cobalt carbonyls, the contents were then heated to 149° and maintained at this temperature for one hour (no absorption of pressure) before cooling and discharging.

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Studies on the Chemistry of Halogens and of Polyhalides. XXII. Halogen Complex Formation and the Taft σ* Constant[1]

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RECEIVED JULY 24, 1962

Formation constants, standard entropies and standard enthalpies for complex formation were determined for a number of compounds in carbon tetrachloride solutions: acetonitrile and monochloroacetonitrile complexes with ICl, IBr and I$_2$, dichloroacetonitrile complexes with ICl and IBr and the trichloroacetonitrile complex with ICl. For each halogen log K was found to be a linear function of the Taft σ* constant. The slopes of log K *vs.* σ* plots were −0.60, −0.43 and −0.32 for ICl, IBr and I$_2$ complexes, respectively. A plot of ΔH^0 *vs.* ΔS^0 for these complexes gave a reasonably straight line, which is characteristic of these donor–acceptor complexes.

Introduction

The classical work of Benesi and Hildebrand[3] on the complexing reaction between iodine and benzene provided a strong impetus toward the studies of molecular complexes involving halogen or interhalogen molecules. During the past decade many such complexes have been investigated primarily by spectrophotometric techniques.[4] It is generally agreed that the halogen

(1) Abstracted from the Ph.D. Dissertation of William C. Golton, State University of Iowa, June, 1962.

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(3) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

(4) (a) L. J. Andrews and R. M. Keefer in "Advances in Inorganic Chemistry and Radiochemistry," Vol. III, H. J. Emeléus and A. G. Sharpe, Editors, Academic Press, New York, N. Y., 1961, p. 91; (b) previous papers in this series, see *J. Am. Chem. Soc.*, **83**, 3586 (1961), for paper XXI; (c) R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962); (d) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer Verlag, Berlin, 1961.

complexes are formed by a Lewis acid–base interaction in which the halogen molecule acts as a Lewis acid (or electron acceptor). A large number of Lewis bases with different donor strengths have been used in the studies of halogen complexes. Among them are various substituted aromatic compounds, aromatic and aliphatic amines, amides and nitriles. Halogen complexes differ considerably in their relative strength as shown by their formation constants whose numerical values range from 0.1 to 10^5 (in liter mole^{-1}). The strength of a given complex will depend on the relative acid strength of the halogen molecule and on the electron donor strength of the Lewis base which forms the complex.

It is obvious, of course, that the latter property is closely related to the structure of the donor molecule; however, very little work has been done as yet on the relationship between the structure and the chemical properties of the donors on one hand, and the thermo-