[CONTRIBUTION OF THE BRANCH OF COAL-TO-OIL RESEARCH, BUREAU OF MINES, REGION V]

Kinetics and Mechanism of the Hydroformylation Reaction. The Effect of Olefin Structure on Rate[1]

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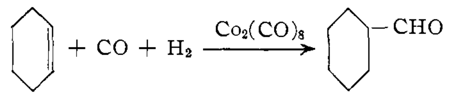
The rate of hydroformylation of alkenes varies in the following manner: straight-chain terminal olefins > straight-chain internal olefins > branched-chain olefins. The position of the double bond in internal unbranched olefins has little or no effect upon the rate. The effect of branching is largest at the carbon atom of the double bond and decreases as the branching occurs further in the chain. There is a minimum in the rate of reaction at the six-membered ring: $C_5 > C_6 < C_7 > C_8$. Double bond isomerization is a slow reaction that occurs to only a small extent under hydroformylation conditions. These results are interpretable on the assumption that a complex between dicobalt octacarbonyl and the olefin is formed in the first step of the reaction and that steric hindrance in the formation of this complex is important. The structure of the olefin-carbonyl complex is discussed.

Olefins with non-conjugated double bonds react with carbon monoxide and hydrogen in the presence of dicobalt octacarbonyl at elevated temperatures and pressures to form the next higher aldehydes.[2] Although the hydroformylation of a large number of olefins has been carried out, no data exist on the relative rates of reaction of various olefins. To obtain information on the mechanism of the hydroformylation reaction, we have studied the effect upon the rate of (1) the position of the double bond and (2) branching in the carbon chain. In addition, we have investigated the effect of various solvents on the rate and clarified the relationship between the hydroformylation reaction and the isomerization of terminal to internal olefins, a reaction which takes place concurrently with the hydroformylation reaction.

Natta and Ercoli[3] have studied the kinetics of the hydroformylation of cyclohexene, using 1:1 synthesis gas ($1H_2$:1CO) at total pressures ranging from 120 to 380 atmospheres; dicobalt octacarbonyl was used as the catalyst. The reaction may be written



(1)

Cyclohexene was chosen for this study because it yields only one aldehyde, hexahydrobenzaldehyde. The rate of hydroformylation was found to be first order with respect to the olefin and approximately proportional to the amount of cobalt present. A number of investigators[4,5] have reported that the rate of hydroformylation increases with increasing hydrogen pressure at constant carbon monoxide pressure and decreases with increasing carbon monoxide pressure at constant hydrogen pressure.

The fact that the rate varies inversely with carbon monoxide pressure had led to the postulation[4] that the first step involves the reaction of the olefin with dicobalt octacarbonyl to form an olefin-carbonyl complex I and carbon monoxide. Martin[5] showed that the following sequence of equations led to a kinetic expression, which fits the data obtained with different ratios of gases at elevated pressures quite well

$$Co_2(CO)_8 + C_6H_{10} \longrightarrow \underset{\text{I}}{Co_2(CO)_7\cdot C_6H_{10}} + CO \qquad (2)$$

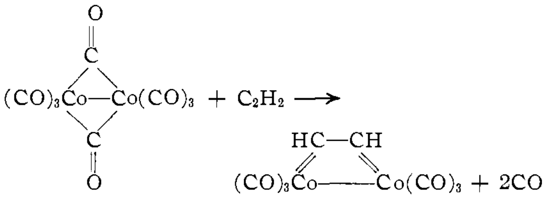
$$Co_2(CO)_7\cdot C_6H_{10} + CO \longrightarrow Co_2(CO)_8 + C_6H_{10} \qquad (3)$$

$$Co_2(CO)_7\cdot C_6H_{10} + H_2 \longrightarrow Co_2(CO)_6 + C_6H_{11}CHO \qquad (4)$$

$$Co_2(CO)_6 + 2CO \longrightarrow Co_2(CO)_8 \qquad (5)$$

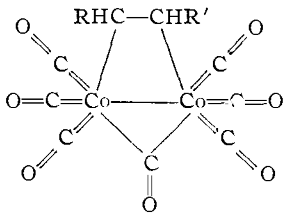
This sequence is similar to that originally suggested[4] except that the reactions shown in equations 2 and 3 are not in equilibrium.

An idea of the structure of I may be gained by examining the complex obtained from the reaction of acetylene with dicobalt octacarbonyl.[6] The stoichiometry of this reaction indicates that the acetylene complex II is formed in the manner



II (6)

The analytical, spectroscopic, magnetic and dipole moment data are compatible with the structure written for II. It is reasonable to assume that an olefin, RCH═CHR′, displaces only one mole of carbon monoxide, so that the olefin-carbonyl complex may have the structure



I

The structure of the olefin will influence the ease of complex formation with dicobalt octacarbonyl. It will be shown that the rates of reaction of various olefins are determined largely by the magnitude of

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[1] Presented in part at the 125th Meeting of the American Chemical Society, Kansas City, Mo., March, 1954.

[2] O. Roelen, U. S. Patent 2,327,066 (Aug. 17, 1943); H. Adkins and G. Kresk, THIS JOURNAL, **70**, 383 (1948); H. Adkins and G. Kresk, *ibid.*, **71**, 3051 (1949); I. Wender, R. Levine and M. Orchin, *ibid.*, **72**, 4375 (1951).

[3] G. Natta and R. Ercoli, *Chimica e Industria*, **34**, 503 (1952).

[4] G. Natta, R. Ercoli, S. Castellano and P. H. Barbieri, THIS JOURNAL, **76**, 4049 (1954); H. Greenfield, S. Metlin and I. Wender, Abstracts of Papers, 126th Meeting of the American Chemical Society, New York, N. Y., September, 1954.

[5] A. R. Martin, *Chemistry & Industry*, 1536 (1954).

[6] H. W. Sternberg, H. Greenfield, R. A. Friedel, J. Wotiz, R. Markby and I. Wender, THIS JOURNAL, **76**, 1457 (1954).

the steric effect involved in the formation of this complex.

Experimental

Materials.—All but one of the olefins used were available from commercial sources, and all were distilled before use. Most of the olefins were obtained from the Phillips Petroleum Co.; their purity was checked by infrared analysis. The following olefins were of 99% minimum purity: 1-pentene, 1-hexene, 1-octene, 2-pentene, 2-heptene and 2,4,4-trimethyl-1-pentene. 2-Hexene, 3-heptene, 2-octene, 2,6-dimethyl-3-heptene, 2-methyl-1-pentene, 4-methyl-1-pentene, 2-methyl-2-pentene, 4-methyl-2-pentene, 2,4,4-trimethyl-2-pentene and 4-methyl-1-cyclohexene were of 95% minimum purity. Cyclopentene, 99.75% purity, and methylcyclohexane, 99% purity, were obtained from the same source. Cyclohexene was purchased from Distillation Products Industries and was chromatographed, using silica gel to remove peroxides. 1-Heptene, 1-decene and 1-tetradecene were obtained from the Humphrey–Wilkinson Co. Camphene was a gift of the Glidden Co. and 2,3,3-trimethyl-2-butene was obtained from the Farchan Co. Cycloheptene came from Columbia Chemicals Co., and the cycloöctene was a gift of the Air Reduction Co. 2,3-Dimethyl-2-butene was synthesized by dehydrating dimethylisopropylcarbinol, using iodine as a catalyst. The mixture of isomeric olefins so obtained was separated by fractional distillation in a column operating at an efficiency of approximately 15 theoretical plates.

The synthesis gas was manufactured at the Bureau of Mines. We are indebted to J. P. Shultz of this Laboratory, who prepared and compressed large amounts of carbon monoxide containing only 0.5% of hydrogen.

The hydroformylation reactions were carried out in a batch system. Experimental conditions were as follows: A solution of 41.0 g. (0.50 mole) of cyclohexene, 65 ml. of methylcyclohexane and 2.8 g. (8.2×10^{-3} mole) of dicobalt octacarbonyl was placed in a 500-ml. no. 347 stainless steel Aminco rocking autoclave. The autoclave and gas compressor were purged three times with 20 atm. of synthesis gas. The unit was filled with 1:1 synthesis gas to cylinder pressure and then boosted to 233 atm., after which the autoclave was isolated from the compressor by a high-pressure valve. The rocking mechanism was started and heat for the autoclave was turned on. It took 56 minutes to heat the autoclave from room temperature to 110°; the temperature was controlled to ±1°. The pressure could be read to within 0.33 atm. on a gage mounted inside the stall. The experiment was continued until the end of the working day, when the heat was turned off and the rocking stopped. A final pressure and temperature reading was taken the following morning. The same autoclave was used for each run.

The reproducibility of the results was examined by conducting duplicate runs and additional runs with cyclohexene at random intervals. A statistical analysis of 55 runs yielded a standard deviation from the mean for the repeated runs of only ±1.5%. The method of least squares was used in calculating the rate constants from the data.

The pressure reading at room temperature was not taken as the initial pressure at room temperature, because there is an appreciable drop after rocking of the autoclave has begun. This pressure drop, which took place before a reaction had begun, did not reach a constant value until the autoclave contents reached a temperature of about 80°. Consequently, the initial pressure at room temperature was calculated from the observed pressures during rocking of the autoclave at elevated temperatures. That gas was taken up by the liquid was demonstrated by making blank runs in the absence of the cobalt carbonyl catalyst. In these runs the initial pressures, which were calculated from observed pressures at elevated temperatures while the autoclave was rocking, were in good agreement with the observed pressures after rocking was stopped and the autoclave had been cooled to room temperature. The initial pressure at reaction temperature, P_0, was then calculated from the calculated initial pressure at room temperature. It was found that approximately 2.2 moles of gas per mole of olefin was utilized; the same value was obtained by Natta and Ercoli[3] for moles of gas absorbed per mole of reacted olefin. This excess gas absorption over the theoretical value of two moles of gas per mole of reacted olefin is probably due to some hydrogenation of the aldehydes and of aldehyde condensation products.

Plots of log ($P_0 - P_f/P_t - P_f$) against time yielded straight lines (P_f = final pressure at reaction temperature at complete reaction, P_t = pressure at time, t), indicating that the rate of decrease of pressure was linear with the total pressure. Several such plots are given in Fig. 1; time corrections for the reaction that occurred on heating to 110° were found by extrapolating conversion *vs.* time plots to zero conversion.

Double Bond Isomerization.—Each experiment was run in the same autoclave using 0.50 mole of either 1-hexene or 2-hexene, 65 ml. of heptane as solvent and 2.8 g. (8.2×10^{-3} mole) of dicobalt octacarbonyl. The amount of hydroformylation was determined from the gas absorption. The reaction product was distilled and the distillate analyzed by infrared spectroscopy for 1-hexene and internal hexenes (2-hexene plus 3-hexene).

Discussion of Results

The rates of reaction of 26 olefinic hydrocarbons at 110° and at 233 atmospheres of 1:1 synthesis gas are listed in Table I. A fifty-fold variation was found between the fastest and slowest rates. The olefins listed in Table I are conveniently divided into five structural classes for purposes of comparison.

TABLE I

RATES OF HYDROFORMYLATION OF OLEFINS AT 110°[a]

		Spec. reacn. rate, $10^3\ k$ min.$^{-1}$ [b]
	A. Straight-chain terminal olefins	
1	1-Pentene	68.3
2	1-Hexene	66.2
3	1-Heptene	66.8
4	1-Octene	65.6
5	1-Decene	64.4
6	1-Tetradecene	63.0
	B. Straight-chain internal olefins	
7	2-Pentene	21.3
8	2-Hexene	18.1
9	2-Heptene	19.3
10	3-Heptene	20.0
11	2-Octene	18.8
	C. Branched terminal olefins	
12	4-Methyl-1-pentene	64.3
13	2-Methyl-1-pentene	7.82
14	2,4,4-Trimethyl-1-pentene	4.79
15	2,3,3-Trimethyl-1-butene	4.26
16	Camphene	2.2
	D. Branched internal olefins	
17	4-Methyl-2-pentene	16.2
18	2-Methyl-2-pentene	4.87
19	2,4,4-Trimethyl-2-pentene	2.29
20	2,3-Dimethyl-2-butene	1.35
21	2,6-Dimethyl-3-heptene	6.22
	E. Cyclic olefins	
22	Cyclopentene	22.4
23	Cyclohexene	5.82
24	Cycloheptene	25.7
25	Cycloöctene	10.8
26	4-Methylcyclohexene	4.87

[a] Conditions: 0.50 mole of olefin, 65 ml. of methylcyclohexane as solvent, 2.8 g. (8.2×10^{-3} mole) of dicobalt octacarbonyl and an initial pressure at room temperature of 233 atmospheres of 1:1 synthesis gas. [b] Every olefin was run at least twice except camphene and cycloöctene, which were run only once.

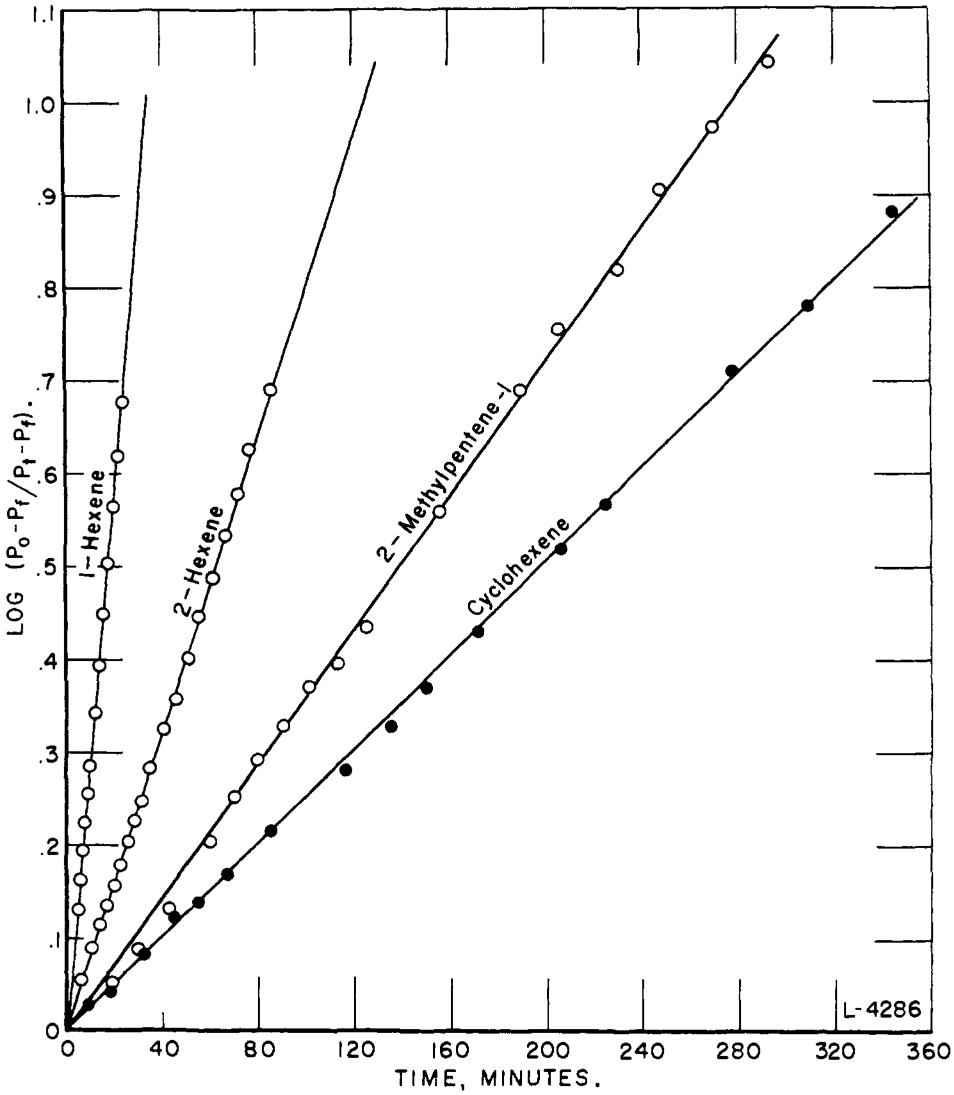


Fig. 1.—Rates of hydroformylation of some olefins at 110° and 233 atm. of equimolar ratios of CO and H_2.

A. Straight-chain Terminal Olefins.—This type of olefin reacts most rapidly. There is a small drop in rate with increase in chain length, but the effect becomes smaller with increase in carbon number. The effect may be due to the increased difficulty of orientation of the double bond in the higher molecular weight olefins with respect to the dicobalt octacarbonyl.

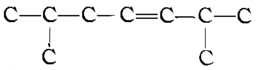
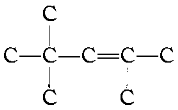
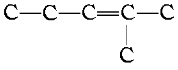
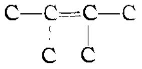
B. Straight-chain Internal Olefins.—The rate of hydroformylation of straight-chain internal olefins is about one-third that of the corresponding terminal olefin. The position of the double bond, as long as it is internal, has little or no effect on the rate; for example, 2-heptene and 3-heptene react at essentially the same speed. These results are interpretable in terms of steric effects in complex formation; the terminal olefinic grouping, $RCH{=}CH_2$, is more accessible than the internal grouping, $RCH{=}CHR$.

C. Branched Terminal Olefins.—Steric interference in complex formation should be greatest for olefins with branching at one of the carbon atoms of the double bond. This is the case, for the largest decrease in rate is obtained by this type of substitution (compare 1-hexene and 2-methyl-1-pentene). Further branching along the chain results in a further decrease in rate; even a single methyl branch on the carbon atom β to the double bond (4-methyl-1-pentene) results in a small but probably significant decrease.

D. Branched Internal Olefins.—Internal olefins that are branched react most slowly. It is clear that a methyl branch at the carbon atom α to the double bond results in a definite decrease in rate (compare 2-hexene and 4-methyl-2-pentene). A glance at the skeletal structures (Table II) of the four remaining branched internal olefins reveals that the differences in rates of reaction are explainable again in terms of steric hindrance, probably in complex formation.

Although 2,6-dimethyl-3-heptene is highly branched and has a double bond farthest removed from the terminal position, it reacts most rapidly because there are no substituents directly on the double bond to offer steric interference to complex formation with the carbonyl. It is seen that the other

TABLE II

Olefin	$10^3 k$., min.$^{-1}$	Olefin	$10^3 k$., min.$^{-1}$
 $\mathrm{C{-}C(C){-}C{-}C{=}C{-}C(C){-}C}$	6.2	 $\mathrm{C{-}C(C)(C){-}C{=}C(C){-}C}$	2.3
 $\mathrm{C{-}C{-}C(C){=}C{-}C}$	4.9	 $\mathrm{C{-}C(C){=}C(C){-}C}$	1.4

olefins offer increased steric hindrance at the site of reaction and react at correspondingly decreased rates.

E. Cyclic Olefins.—Since all cyclic olefins are internal olefins, they may be compared with the straight-chain internal olefins. It appears reasonable to assume that there is no greater steric hindrance involved in the formation of a complex between an unbranched cyclic olefin and dicobalt octacarbonyl than in the formation of a similar complex with a straight-chain internal olefin. However, the rate of reaction of cyclohexene is slow, suggesting that the other steps of the reaction, that is, further reaction of the intermediate complex I, do not proceed very rapidly.

The importance of the other step or steps of the reaction in determining the rate of hydroformylation of various olefins is seen when the relative rates of reaction of the cyclic olefins presented in Table I are examined. Steric effects in the formation of complexes with catalyst by the olefin are probably comparable, yet there are large variations in rates.

The fact that a minimum in the rate of reaction of the cyclic olefins occurs at the C_6-ring is not wholly unexpected; a similar relationship between the chemical reactivity of saturated rings and ring size has been obtained for two different types of reactions by Prelog[7] and Brown and Borkowski.[8] Since cyclic olefins are more strained than the corresponding saturated rings, it is reasonable to expect that the rate of reaction of the olefin–carbonyl complex will be influenced by the magnitude of the internal strain in the olefin. Beckett, Freeman and Pitzer[9] have calculated the strain energy of cyclopentene to be 9.8 kcal./mole, that of cyclohexene 1.6 kcal./mole. While the greater rate of reaction of cyclopentene can thus be explained, the reasons for the relative rates of cycloheptene and cycloöctene are less obvious. Schubert and Sweeney[10] have obtained evidence that cycloheptene rings are strained from a consideration of the ultraviolet spectra of α,β-unsaturated carbonyl groups. These workers have pointed out that an examination of Fisher–Taylor–Hirschfelder models indicates that the degree of hydrogen crowding is much more pronounced in cycloheptene derivatives than in cyclohexene derivatives. The results obtained in this work would indicate that the relief of strain in the saturation of cycloheptene is perhaps greater than the corresponding strain relief for cyclopentene or cycloöctene.

The Effect of Solvents.—The hydroformylation reaction has been carried out in a variety of solvents, but heretofore no data on the effect of the solvent on the rate of the reaction have been reported. The effect of the solvent on the rate of hydroformylation of cyclohexene at 110° and 233 atmospheres of 1:1 synthesis gas is shown in Table III.

TABLE III

EFFECT OF SOLVENTS ON THE RATE OF HYDROFORMYLATION OF CYCLOHEXENE AT 110°

Solvent	Spec. reacn. rate, 10^3k, min.$^{-1}$	Solvent	Spec. reacn. rate, 10^3k, min.$^{-1}$
Methylcyclohexane	5.8 ± 0.1	Chlorobenzene	6.5 ± 0.1
Heptane	5.9	Benzene	6.7
Methyl ethyl ketone	5.7	Anisole	7.5
n-Butyl ether	5.9	α-Methylnaphthalene	7.9
Acetone	6.1	Ethanol	8.7
2-Ethylhexanol-1	6.5	Methanol	8.9

The solvent effect is not large, although it appears to be significant; the rate is increased about 1.5 times in going from a saturated hydrocarbon to methanol or ethanol.[11] The rate in aromatic solvents is enhanced; this effect may be due to the polarizability of the aromatic molecule or to the fact that aromatic hydrocarbons are very weak bases.[12] Whatever the cause, it does not appear likely that highly polar intermediates are involved in the hydroformylation reaction.

Double Bond Isomerization.—When a terminal olefin is hydroformylated, part of the olefin is converted to aldehydes and part is isomerized to internal olefins. However, the hydroformylation of an internal olefin must involve a movement of the double bond to the terminal position, for the aldehydes obtained are chiefly derived by addition of the formyl group to the terminal carbons. To understand the mechanism of the reaction, these facts must be reconciled with the results of the kinetic studies on various olefins.

We shall consider, first, the double bond isomerization which occurs under hydroformylation conditions. Asinger and Berg[13] found that 1-dodecene was isomerized to a mixture which consisted of all the possible double bond isomers in almost equal ratios when the olefin was treated with either a Fischer–Tropsch cobalt catalyst or cobalt metal for one hour at temperatures between 150 and 250° and at 100 atmospheres pressure of car-

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[7] V. Prelog, *J. Chem. Soc.*, 423 (1950).

[8] H. C. Brown and M. Borkowski, THIS JOURNAL, **74**, 1894 (1952).

[9] C. W. Beckett, N. K. Freeman and K. S. Pitzer, *ibid.*, **70**, 4227 (1948).

[10] W. M. Schubert and W. A. Sweeney, *ibid.*, **77**, 2297 (1955).

[11] Methanol and ethanol react with dicobalt octacarbonyl at room temperature and atmospheric pressure according to the equation (see I. Wender, H. W. Sternberg and M. Orchin, *ibid.*, **74**, 1216 (1952)): $3[Co(CO)_4]_2 + 12\ ROH \rightarrow 2Co[(ROH)_6][Co(CO)_4]_2 + 8CO$. The solution of the salt is light red in each case. However, the solution at the end of a run in which one of these alcohols has been used as a solvent is dark red-black and evolves carbon monoxide on standing. There is no doubt that the above reaction is reversed at high pressures of carbon monoxide and that essentially all of the cobalt is converted to dicobalt octacarbonyl under reaction conditions.

[12] Preliminary work by the present authors has shown that the rate of hydroformylation of cyclohexene is increased by the addition of small amounts of organic bases and inhibited by larger amounts. It is not likely that the variations in specific reaction rates with solvent are a reflection of the difference in solubility of hydrogen and carbon monoxide in the reaction media; hydrogen, for instance, is more soluble in paraffins than in aromatics of similar molecular weight. See M. R. Dean and J. W. Tooke, *Ind. Eng. Chem.*, **38**, 389 (1946).

[13] P. Asinger and O. Berg, *Ber.*, **88**, 445 (1955).

bon monoxide. In the present work, 1-hexene was heated at 110° for one hour in the presence of dicobalt octacarbonyl and 133 atmospheres of carbon monoxide; 9% of the 1-hexene was converted to internal hexenes under these conditions. When the temperature was raised to 150° under the same conditions, 29% of the terminal olefin was isomerized to internal olefins. The yield of 2-hexene and 3-hexene increased to 61% when 1-hexene was heated at 150° for 5 hours. Only traces of 1-hexene were formed when 2-hexene was treated in a similar manner. It thus appears that dicobalt octacarbonyl readily catalyzes the isomerization of terminal olefins and that the extent of isomerization increases with temperature and time.[14] The shifting of the double bond probably occurs when the olefin–cobalt carbonyl complex dissociates to form olefin and octacarbonyl (see equation 3).

When hydroformylation of a terminal olefin is interrupted and the unreacted olefin examined, it is found that most of the recovered olefin has been isomerized to internal olefins.[15] In the present work, 1-hexene was heated to 110° with 233 atmospheres of 1:1 synthesis gas and then cooled to room temperature; 75% of the olefin reacted to form aldehydes; the remaining olefin consisted of 84% of a mixture of 2-hexene and 3-hexene and 16% of 1-hexene. We may conclude, therefore, that extensive double bond isomerization does not occur under hydroformylation reaction. The hydroformylation of 1-hexene is faster than that of 2- or 3-hexene and there is an accumulation of internal olefin during the reaction. The fact that 1-hexene is recovered as such and that 1-hexene reacts more rapidly than the 2-olefin indicates that the isomerization of double bonds under hydroformylation conditions is slower than hydroformylation.

When the hydroformylation of 2-hexene at 110° and 233 atmospheres of synthesis gas was terminated before completion, no 1-hexene was found in the reaction products.

The Nature of the Cobalt Carbonyl–Olefin Complex.—Although internal olefins are thermodynamically more stable than terminal olefins under reaction conditions, the products obtained in the hydroformylation reaction, as mentioned above, are largely derived by addition to the terminal carbons. For example, the distribution of alcohols secured from 1-pentene and 2-pentene is about the same[16]; 50 to 55% of *n*-hexyl alcohol, 35 to 40% of 2-methylpentanol-1 and 10% of 2-ethylbutanol-1. In each case, the chief product can only be obtained by the addition of the formyl group to the number one carbon atom.

These facts may be explained in the following manner, using 1-pentene and 2-pentene as examples: Because of steric hindrance, 2-pentene reacts with dicobalt octacarbonyl to form a complex more slowly than 1-pentene and this accounts for the differences in rates observed with these olefins. It appears that the energy required for the rearrangement of the complex subsequent to its initial formation is small; we may therefore conclude that essentially the same complex is obtained from both terminal and internal olefins.

The structure given for the olefin–carbonyl complex I probably represents the complex as it initially forms from either a terminal or internal olefin. It is not possible at present to write an adequate structure for the olefin–carbonyl complex as it exists a moment later, for the position of attachment of the unsaturated entity to the carbonyl is probably not fixed.[17]

BRUCETON, PENNA.

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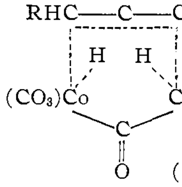
[14] The small amount of hydrogen (0.5%) in the carbon monoxide can have no marked effect on double bond isomerization. Isomerization is not fast even when very large amounts of hydrogen are added. To show that isomerization occurs in the absence of hydrogen, dicobalt octacarbonyl was refluxed in 1-hexene until complete conversion to the tricarbonyl, $[Co(CO)_3]_4$, took place; 5% of the olefin was isomerized after this time. No isomerization took place when 1-hexene was refluxed with $[Co(CO)_3]_4$.

[15] I. Wender, H. W. Sternberg and M. Orchin, THIS JOURNAL, **75**, 3042 (1953); G. Natta, R. Ercoli and S. Castellano, *Chimica e Industria*, **37**, 6 (1955).

[16] A. I. M. Keulemans, A. Kwantes and T. van Bavel, *Rec. trav. chim.*, **67**, 298 (1948); E. A. Naragon, A. J. Millendorf and L. P. Larson, paper presented at the Houston, Texas, Meeting of the American Chemical Society, March, 1950.

[17] Some mechanism must exist for the facile movement of hydrogen along the carbon chain. R. B. Anderson, of this Laboratory, has suggested that hydrogen atoms are transferred from one part of the molecule to the other by interaction with the cobalt atoms. We may perhaps write the following structure to indicate a manner in which the olefin may be bonded in complex (a). It is interesting that allenes,



(a)

$RCH{=}C{=}CH_2$ are polymerized by dicobalt octacarbonyl at room temperature (see H. Greenfield, I. Wender and J. Wotiz, *J. Org. Chem.*, **21**, 875 (1956).