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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

The Stoichiometric Hydroformylation of 1-Pentene at Room Conditions[1]

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A series of hydroformylation reactions of 1-pentene with cobalt hydrocarbonyl using various concentrations of olefin and cobalt hydrocarbonyl was conducted at atmospheric pressure at 0° and 25° employing either carbon monoxide or nitrogen atmospheres. By controlling conditions it is possible to obtain yields of aldehyde varying from essentially zero to about 70%; to change the distribution of isomeric aldehydes from about 80% straight chain to about 95% branched chain; to convert the excess 1-pentene practically completely to 2-pentene or to leave it unaffected. In general, the presence of carbon monoxide both above the reaction mixture and in solution retards both the hydroformylation and the isomerization of olefin.

It is well known that the conventional oxo synthesis can be catalyzed by adding any form of cobalt to the charge in the high pressure vessel. Since the report of experiments demonstrating that cobalt is present under catalytic hydroformylation conditions[2] as cobalt hydrocarbonyl, $HCo(CO)_4$, increasing interest has centered around the stoichiometric reaction[3] between olefins and cobalt hydrocarbonyl. Previous work in this laboratory[4] has shown that with only a moderate excess of a 1-olefin under one atmosphere of carbon monoxide, the stoichiometry of the reaction is:

$$2\ HCo(CO)_4 + CO + \text{olefin} \longrightarrow Co_2(CO)_8 + \text{aldehyde} \qquad (1)$$

However, Heck and Breslow have shown,[5] that in the presence of a large excess of olefin the absorption of carbon monoxide approaches one mole of carbon monoxide per mole of cobalt hydrocarbonyl. They further showed that the complex formed from one cobalt hydrocarbonyl:carbon monoxide:olefin, one of the complexes previously suggested as an intermediate,[4] was a distinct isolable compound, namely, an acylcobalt tetracarbonyl, $RCOCo(CO)_4$. It is, accordingly, now evident that aldehyde product may be accounted for by the following over-all reaction:

$$R{-}CH{=}CH_2 + HCo(CO)_4 + CO \longrightarrow RCH_2CH_2COCo(CO)_4 \xrightarrow{HCo(CO)_4} CO_2(CO)_8 + RCH_2CH_2CHO \qquad (2)$$

and that reaction (1) represents the stoichiometry of aldehyde production in the presence of a moderate excess of olefin where the acylcobalt tetracarbonyl formation is slow relative to its cleavage by hydrocarbonyl. In the presence of a very large excess of olefin, the cobalt hydrocarbonyl is practically all converted to the acylcobalt tetracarbonyl and little is available for cleavage. This is also the probable explanation for the absence of free hydrocarbonyl during the course of the catalytic hydroformylation and its appearance only after most of the olefin is consumed.[2]

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(1) Presented in part before the Organic Division, 137th Meeting American Chemical Society, Cleveland, Ohio, April 1960, and in part before the Physical Division at the 139th Meeting of the American Chemical Society, St. Louis Mo., March 1961.

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

(3) The room temperature, atmospheric pressure reaction, in which cobalt hydrocarbonyl is consumed stoichiometrically and is not regenerated will be called the stoichiometric hydroformylation whereas the hydroformylation conducted under the so-called oxo conditions (110°–175°; 200–400 atm. carbon monoxide:hydrogen) and in which a small quantity of cobalt converts a large quantity of olefin to aldehyde will be called the catalytic hydroformylation.

(4) L. Kirch and M. Orchin, *J. Am. Chem. Soc.*, **81**, 3597 (1959).

(5) R. F. Heck and D. S. Breslow, *Chem. and Ind.*, **17**, 467 (1960).

One of the most remarkable aspects of the stoichiometric hydroformylation in the presence of excess 1-olefin, is the recovery of isomerized olefin.[2,6] It is the purpose of the present paper to report on a study of such isomerizations as well as on the distribution of aldehydic products which result from changes in the relative and absolute concentrations of the reactants in the stoichiometric hydroformylation of 1-pentene.

RESULTS AND DISCUSSION

Cobalt hydrocarbonyl was prepared by the disproportionation of cobalt tetracarbonyl by dimethylformamide (DMF).[7] Hexane solutions usually containing four mmoles of cobalt hydrocarbonyl were employed and all reactions were conducted in a closed gasometric system[8] under carbon monoxide or nitrogen. At the conclusion of the desired reaction time, either quinoline or dimethylformamide was injected in order to remove cobalt hydrocarbonyl. Most of the olefin was recovered by vacuum distillation and then analyzed by vapor phase chromatography (MPC). Water was then added to the quenched reaction mixture and the hydrocarbon phase sampled and analyzed by VPC.

Effect of carbon monoxide. Remarkable differences in rate and product distribution occur, depending upon whether the hydroformylation is conducted under 1 atm. of carbon monoxide or of nitrogen (Table I). At 0°, for example, no detectable reaction occurs under carbon monoxide, but under nitrogen, with conditions otherwise identical, the reaction is over at the end of at least 15 min. Obviously, carbon monoxide inhibits the reaction at 0°. However, at 25°, under carbon monoxide, the reaction is essentially complete—*i.e.* all the cobalt hydrocarbonyl has disappeared—after 3 min. The carbon monoxide inhibition must be due to the suppression of the formation of an intermediate or a transition state; the difference in rate caused by a 25° change in temperature would lead to an impossibly high energy of activation if the same species were present at both temperatures.

TABLE I

1-PENTENE + COBALT HYDROCARBONYL—EFFECT OF CARBON MONOXIDE (30 MIN.)

			Aldehyde		Pentene		
1-P/Co[a]	Gas	Temp.	Tot.	B/S[b]	1-	2-	t/c[c]
25	N_2	25	39	2.6	48	52	0.9
25	CO	25	37	2.2	65	35	0.8
2	N_2	25	7	>25	10	90	5.4
2	CO	25	53	0.3	98	2	—
25	N_2	0	31	2.4	51	49	0.8
25	CO	0	No reaction				

[a] Ratios of mmoles of 1-pentene/mmoles of $HCo(CO)_4$. [b] Branched/straight chain. [c] *trans/cis*.

If, instead of employing 100 mmoles of 1-pentene and four mmoles of cobalt hydrocarbonyl (25:1) only eight mmoles of 1-pentene is treated with the same quantity of cobalt hydrocarbonyl (1-P/Co=2), vastly different results are obtained. The aldehyde yield under nitrogen is sharply reduced by the reduced 1-pentene:cobalt ratio and the product is almost exclusively the branched-chain aldehyde. The recovered olefin is almost all 2-pentene, and the *trans*-isomer predominates. On the other hand, under carbon monoxide the reduced 1-pentene:cobalt ratio results in an increased yield of aldehyde, the majority of which (77%) is straight chain, and the recovered olefin is almost completely the original one. Although exact data are lacking, the rate of cobalt hydrocarbonyl disappearance is definitely slower with the smaller concentration of 1-pentene.

In considering possible explanations for these facts it became apparent that not only was the total quantity of olefin of importance but that the concentration of olefin was of even greater significance. The first three experiments listed in Table II were performed with a constant 1-pentene:cobalt ratio, but the reactants were successively diluted with increasing quantities of solvent hexane. With increasing dilution, the yield of aldehyde increased although the rate of reaction fell off. The effect of increasing the total volume, among other things, is to increase the concentration of dissolved carbon monoxide relative to the reactants. One possible conclusion that may be drawn from these results is that the olefin and the dissolved carbon monoxide compete for the cobalt in a nucleophilic displacement of one of the carbon monoxide ligands on the cobalt hydrocarbonyl. At low olefin concentration, olefin-carbonyl complex concentration is low because of carbon monoxide competition for the cobalt. The olefin carbonyl complex under the influence of the carbon monoxide, rapidly rearranges to an acylcobalt compound[5] which can then react with uncomplexed

TABLE II

EFFECT OF CONCENTRATION OF 1-PENTENE (4 MMOLES OF COBALT HYDROCARBONYL; CARBON MONOXIDE; 25°)

Tot. Vol. Ml.	1-P/Co	1-P Mm./Ml.	Aldehydes Tot., %		Pentenes, %		Time, Min.[a]
				B/S	1-	2-	
12	5	1.50	34	1.1	88	12	12
32	5	.56	42	0.6	100	—	45
52	5	.35	62	0.6	100	—	65
11	1.2	.43	67	0.3	99	—	

[a] Approx. time required for CO absorption to cease.

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(6) I. Wender, H. W. Sternberg, and M. Orchin, *J. Am. Chem. Soc.*, **75**, 3041 (1953).

(7) L. Kirch and M. Orchin, *J. Am. Chem. Soc.*, **80**, 4428 (1958).

(8) M. Orchin and I. Wender, *Anal. Chem.*, **21**, 875 (1949).

cobalt hydrocarbonyl leading to aldehyde in high yield with little concomitant isomerization. If the stoichiometric hydroformylation is carried out under 4 atm. of carbon monoxide, the rate is slow, the ultimate yield of aldehyde is high, and no isomerization occurs.

Variations in reaction conditions in the presence of nitrogen (Table III) lead to quite different products as compared to a carbon monoxide atmosphere. Under nitrogen, the stoichiometry of aldehyde formation obviously cannot be represented by equation (2) since the sole source of the carbon in the carboxaldehyde group must be the cobalt hydrocarbonyl. The stoichiometry and the fate of the cobalt have not been established in this reaction. The decrease in 1-pentene:cobalt ratio shown in Table III results in increasing the cobalt hydrocarbonyl concentration as well as increasing the cobalt:1-pentene ratio. The drop-off in yield of aldehyde possibly results from the frequency of complex formation and dissociation under these conditions since neither of the nucleophilic species, carbon monoxide or olefin, is present to rearrange the complex to products. Extensive isomerization accordingly, should occur.

TABLE III

EFFECT OF 1-PENTENE:COBALT HYDROCARBONYL RATIO
NITROGEN, 0°, 30 MIN.

	Aldehyde		Pentenes		
1-P/Co	Tot. %	B/S	1-	2-	t/c
25	31	2.4	51	49	0.8
4.5	16	1.8	3	97	5.2
4.3			3	97	5.2
2	6	>25	7	93	3.7

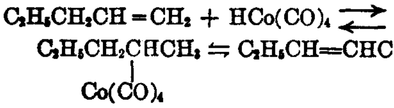
Isomerization. Under certain conditions, especially in the absence of carbon monoxide, cobalt hydrocarbonyl is a very efficient isomerization catalyst. Thus, in the first experiment listed in Table I, 52% of the recovered olefin had been isomerized. In this experiment, all the cobalt hydrocarbonyl had disappeared after a few minutes yet the four mmoles of cobalt hydrocarbonyl had isomerized over fifty mmoles of olefin during this time. Increasing the carbon monoxide concentration, in general, decreases the extent and rate of isomerization. The data in Table IV show that *cis*-2-pentene in the presence of nitrogen is isomerized to the *trans*, but even at higher temperatures, the presence of carbon monoxide inhibits the *cis*→*trans* isomerization. The high yield of aldehyde under carbon monoxide and the ratio of isomeric aldehydes suggest that isomerization of the *cis*-2-pentene to 1-pentene occurs, and that the latter is then hydroformylated.

One of the most simple and attractive reaction schemes for explaining the isomerization of the olefin consists of Markovnikoff addition of cobalt hydrocarbonyl to the olefin, followed by splitting out of the cobalt hydrocarbonyl according to the equilibria of Equation 3. However, under conditions which should maximize the concentration of alkylcobalt tetracarbonyl (nitrogen, large excess of olefin) no evidence for an equilibrium concentration of cobalt hydrocarbonyl was found. Furthermore, ethylcobalt tetracarbonyl[5] should have an equilibrium concentration of ethylene above it, Equation 4, but no evidence for ethylene was found. In addition, treatment of cobalt hydrocarbonyl with excess ethylene (starting with the right side of Equation 4) in the absence of any other gas resulted in complete disappearance of cobalt hydrocarbonyl indicating again that Equation 4 is not an equilibrium. There appears to be no evidence that $RCo(CO)_4$ once formed, dissociates into its components under conditions of the stoichiometric hydroformylation.

TABLE IV

EFFECT OF PENTENE STRUCTURE
NITROGEN, 0°, 30 MIN., P/CO = 2

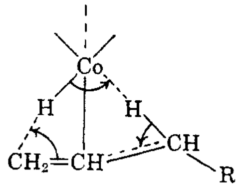
	Aldehydes		Pentenes		
Pentene	Tot. %	B/S	1-	2-	t/c
1-P	6	>25	7	93	3.7
cis–2-P	6		8	92	2.0
	CO, 25°,	P/Co = 2			
cis-2-P	31	0.8	6.0	94	0.07



$$C_2H_5CH_2CH=CH_2 + HCo(CO)_4 \rightleftarrows \underset{\displaystyle Co(CO)_4}{C_2H_5CH_2\overset{|}{C}HCH_3} \leftrightarrows C_2H_5CH{=}CHCH_3 + HCo(CO)_4 \quad (3)$$

$$CH_3CH_2Co(CO)_4 \rightleftarrows HCo(CO)_4 + CH_2{=}CH_2 \quad (4)$$

Although a final answer to the mechanism of the isomerization cannot be advanced as yet, one attractive possibility which rationalizes much of the existing data consists of coordination of the olefin with cobalt hydrocarbonyl in an S_m2 type of transition state followed by an allylic proton shift and dissociation. The transition state may be represented as follows:



Investigations with cobalt deuterocarbonyl now under way in this laboratory may prove decisive in establishing the olefin-isomerization mechanism.

EXPERIMENTAL

Preparation of cobalt hydrocarbonyl. One neck of a 250-ml. two-neck flask was connected to a 500-ml. buret and the other closed with a serum stopper. After purging with the carbon monoxide, 10 ml. of 0.3*M* dicobalt octacarbonyl in hexane was syringed into the flask followed by 3 ml. of dimethylformamide. After the evolution of carbon monoxide ceased (30 min.), the mixture was cooled to 0° and 6 ml. of 12*N* hydrochloric acid added dropwise with (magnetic) stirring. The lower layer was syringed off and the remaining 0.4*M* cobalt hydrocarbonyl in hexane washed with 10 ml. of oxygen-free water. In the experiments where a nitrogen atmosphere was desired, the system was purged with nitrogen at this point. If, anhydrous cobalt hydrocarbonyl was desired, the solution was cooled to −70° and the hexane solution syringed off the ice and transferred to another flask under carbon monoxide or nitrogen as desired.

Hydroformylation. To the 0.4*M* solution of cobalt hydrocarbonyl, prepared as described above, the desired quantity of pentene was added and the solution stirred for the desired time. In the experiments in which the total volume was of interest (Table II) the pentene was diluted with the appropriate volume of hexane; otherwise the total volume was 10 ml. plus the volume of added pentene. At the end of the reaction time, 3 ml. dimethylformamide or 2 ml. of quinoline was added, and the mixture stirred until evolution of carbon monoxide stopped. Two milliliters of reaction mixture was then slowly distilled under vacuum with stirring into a test tube at −70° and the material collected was used for vapor phase chromatography analysis for olefins. To the residue, 20 ml. of water was added, and after stirring the mixture for 5 min., the hydrocarbon layer was sampled for aldehyde analysis by vapor phase chromatography. The data are summarized in the tables in the text.

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CINCINNATI 21, OHIO

[CONTRIBUTION FROM ROHM & HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION]

The Structure of Pernitroso Compounds of *t*-Alkyl Ketones[1]

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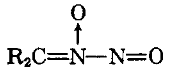
The nitrimine structure, $R_2C{=}N{-}NO_2$, previously proposed for the so-called pernitroso compounds derived from *t*-alkyl ketoximes, is supported by infrared and ultraviolet spectral evidence and by the conversion of these compounds to primary nitramines with complex hydrides.

The reaction of ketoximes with nitrosating agents to regenerate the parent ketone has been used extensively as a synthetic tool but the course of the reaction and the nature of the intermediates are only partly understood.[2,3] In a few instances, pseudonitroles are produced.[4] In most cases the intermediates are not isolated but decompose under the conditions of the reaction to ketone and nitrous oxide.[5] However, certain terpenoid and steroid ketoximes yield pernitroso compounds[6] which can be isolated and which in turn are convertible to the parent ketones by hydrolysis.[6a] The distinguishing characteristic of pernitroso compounds prepared by this reaction is the presence of a tertiary alkyl group attached to the oximino group; the stability of these compounds apparently depends upon this group.[7,10]

A number of structural formulas have been suggested for these compounds. The Italian school originally proposed the oxime nitrite structure (I)

$R_2C{=}N{-}ONO$

I

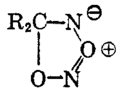


$$R_2C{=}\overset{\overset{\displaystyle O}{\uparrow}}{N}{-}N{=}O$$

II

$R_2C{=}N{-}NO_2$

III



IV

which was subsequently abandoned in favor of the *N*-nitrosooxime formulation (II).[11] This latter formulation was favored by Fusco and his co-

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[1] This research was carried out under Army Ordnance Contract DA-01-021-ORD-11878.

[2] D. T. Manning and H. A. Stansbury, Jr., *J. Am. Chem. Soc.*, **81**, 4885 (1959). This article contains a good bibliography of this reaction.

[3] (a) Aldoximes undergo more complicated reactions including oxidation and nitration [J. H. Boyer and H. Alul, *J. Am. Chem. Soc.*, **81**, 4237 (1959)]. (b) Recently it has been shown that azine bisoxides are common oxidation products of aromatic aldoximes [L. Horner, L. Hockenberger, and W. Kirmse, *Chem. Ber.*, **94**, 290 (1961)].

[4] R. Scholl, *Ber.*, **18**, 507 (1885).

[5] A few steroid ketoximes yield nitrogen rather than nitrous oxide.

[6] Pernitroscocamphor was obtained along with camphor from the reaction of the sodium salt of camphor oxime and perchloryl fluoride. The appearance of this material confirms the suggestion that nitrosating agents are produced during this reaction [J. P. Freeman, *J. Am. Chem. Soc.*, **82**, 3869 (1960)].

[6a] For example, see A. Gandini, *Gazz. chim. ital.*, **72**, 232 (1942).

[7] The only known exception to this rule is that of pernitrosomesityl oxide.[8] Its structure has been shown[9] to be different from that of the pernitroso compounds discussed in this article.

[8] C. Harries and R. Gley, *Ber.*, **32**, 1330 (1899).

[9] J. P. Freeman, to be published.

[10] A number of new compounds containing the pernitroso group have been prepared by the action of nitric oxide on azine bisoxides.[3b] The nitrimine structure (III) was assigned on the basis of spectral and chemical properties. Under the nonhydrolytic conditions of this reaction, these nitrimines, which do not possess *t*-alkyl groups, survive.

[11] O. Angelucci, *Ann.*, **341**, 172 (1905).