[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMICAL ENGINEERING AND CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

Synthesis of Olefin Hydrocarbons by Catalytic Condensation and Dehydration of Aliphatic Aldehydes

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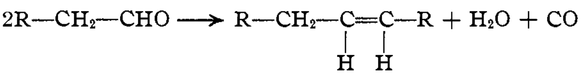
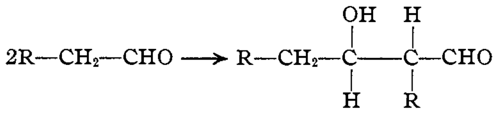
In recent articles[1] a catalytic method was presented for the preparation of ketones from primary alcohols by condensation over chromium oxide at 400° and atmospheric pressure. The mechanism suggested was as follows: (1) dehydrogenation to the aldehyde, (2) aldol condensation, (3) removal of carbon monoxide from the carbonyl group of the aldol leaving a secondary alcohol, (4) dehydrogenation of this alcohol to the ketone. This mechanism was supported by the fact that the degree of conversion to the ketones was aldol > aldehyde > alcohol. It was of interest to elucidate this reaction further, so a study of the effect of pressure was undertaken. Since aldehydes gave better yields than alcohols in the above reaction, and were also more available than aldols, they were used in the following pressure experiments.

Under super-atmospheric pressure the reaction proceeds in a different manner. The aldol condensation is followed by *dehydration rather than dehydrogenation*, and is accompanied by a loss of carbon monoxide, which results in the formation of olefin hydrocarbons. The over-all reaction is

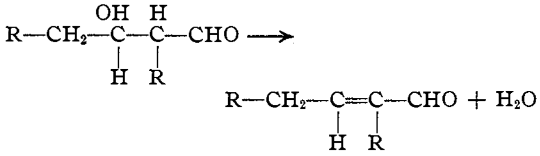


$$2R{-}CH_2{-}CHO \longrightarrow R{-}CH_2{-}\underset{H}{C}{=}\underset{H}{C}{-}R + H_2O + CO$$

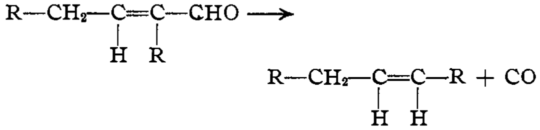
The probable mechanism for the reaction is

(1) 

$$2R{-}CH_2{-}CHO \longrightarrow R{-}CH_2{-}\overset{OH}{\underset{H}{C}}{-}\overset{H}{\underset{R}{C}}{-}CHO$$

(2) 

$$R{-}CH_2{-}\overset{OH}{\underset{H}{C}}{-}\overset{H}{\underset{R}{C}}{-}CHO \longrightarrow R{-}CH_2{-}\underset{H}{C}{=}\underset{R}{C}{-}CHO + H_2O$$

(3) 

$$R{-}CH_2{-}\underset{H}{C}{=}\underset{R}{C}{-}CHO \longrightarrow R{-}CH_2{-}\underset{H}{C}{=}\underset{H}{C}{-}R + CO$$

This mechanism was indicated by the isolation of the unsaturated aldehyde formed in step (2).

Propionaldehyde, *n*-butyraldehyde, *n*-amyl aldehyde and *n*-hexaldehyde were subjected to the action of a chromium oxide catalyst at temperatures between 330 and 410° and super-atmospheric pressures.

At temperatures between 385 and 410° the predominant reaction is olefin formation as shown in step (3) of the proposed mechanism. From propionaldehyde, *n*-butyraldehyde, *n*-amyl aldehyde and *n*-hexaldehyde the corresponding olefins, free from any impurities, are produced: namely, pentene-2, heptene-3, nonene-4 and undecene-5, in yields of 40–50% of theoretical.

In a lower temperature range (330–365°) step (2) is the predominant reaction. The unsaturated aldehydes which are, in fact, α,β substituted acroleins can be obtained in 40% yields. If hydrogen is used to build up the initial pressure, hydrogenation of the active olefin bond occurs, producing substituted, saturated aldehydes.

It is of interest to note that when one of the most effective dehydrating catalysts, aluminum oxide, was used the results obtained were not as good as those using pure chromium oxide. A control experiment using no catalyst gave only unchanged aldehyde with traces of decomposition products. By using a complex action catalyst (chromium oxide–nickel)[2] and a higher initial pressure of hydrogen, the saturated hydrocarbon and the saturated aldehyde can be obtained exclusively.

The aldol condensation which occurred was not limited to two molecules of the aldehyde. Evidence was obtained for reactions involving the condensation of three or more molecules.

The probable mechanism involves a multiple aldol condensation with subsequent loss of water and carbon monoxide. The isolation of the hydrocarbons corresponding to a condensation of three molecules of the aldehyde was effected in experiments using propionaldehyde and *n*-butyraldehyde, namely, an iso-octene and iso-undecene.

Experimental Part

Apparatus and Procedure.—The experiments were carried out in a high pressure rotating autoclave equipped

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(1) V. I. Komarewsky and J. R. Coley, THIS JOURNAL, 63, 700, 3269 (1941).

(2) Chromium oxide functions as a condensation catalyst and nickel as a hydrogenation catalyst.

TABLE I

Aldehyde charge	Catalyst	Initial pressure, atm.	Max. temp., °C.	Yield of olefin, %	Yield of aldehyde, %	
					Unsatd.	Satd.
Propionaldehyde	Cr_2O_3	20 N_2	400	40[a]	18.7[b]	0
Butyraldehyde	Cr_2O_3	20 H_2	400	51[c]	4.0[d]	4.9[e]
Butyraldehyde	Cr_2O_3	20 H_2	365	35	15.5	10.4
Butyraldehyde	Cr_2O_3	20 H_2	330	6	40.2	8.1
Butyraldehyde	Cr_2O_3	20 N_2	360	15	45	0
Butyraldehyde	None	20 H_2	402	0	0	0
Amylaldehyde	Cr_2O_3	20 N_2	400	32[f]	..	..
Hexaldehyde	Cr_2O_3	20 H_2	408	39[g]	..	..
Butyraldehyde	Al_2O_3	20 N_2	400	17	15	0
Butyraldehyde	Cr_2O_3–Ni	40 H_2	400	50[h]	0	20

[a] *cis–trans*-Pentene-2, b. p. 36–37° d^{17} 0.656, n^{20}_D 1.3775. [b] 2-Methyl-3-ethylacrolein, b. p. 136°: derivative, 2,4-dinitrophenylhydrazone, m. p. 160°. [c] *cis–trans*-Heptene-3, b. p. 95.8–96.0°, d^{20} 0.7010, n^{22}_D 1.4039; derivative, *n*-heptane, b. p. 98°, d^{20} 0.685. [d] 2-Ethyl-3-propylacrolein, b. p. 170–173°; derivative, 2,4-dinitrophenylhydrazone, m. p. 124–125°. [e] 2-Ethylhexanal, b. p. 160°; derivative, 2,4-dinitrophenylhydrazone, m. p. 114–115°. [f] *cis–trans*-Nonene-4, b. p. 145–148°, d^{18} 0.7330, n^{16}_D 1.4220; derivative, *n*-nonane, b. p. 150–151°, n^{20}_D 1.406. [g] *cis–trans*-Undecene-5, b. p. 187–190°, d^{20} 0.764; derivative, *n*-undecane, b. p. 195–196°, d^{20} 0.7404. [h] Saturated hydrocarbon identified as *n*-heptane, b. p. 98–98.5°, d^{20} 0.685. The olefin corresponding to a second condensation of propionaldehyde was obtained in 10% yield. It was identified as *cis–trans*-4-methylheptene, b. p. 112–115°, n^{22}_D 1.4101; derivative, 4-methylheptane, b. p. 118°, n^{22}_D 1.4000. The olefin corresponding to a second condensation of butyraldehyde was obtained in 5% yield. It was identified as $C_{11}H_{22}$: mol. wt., 153 ± 2; C, 86.26; H, 13.98.

with a glass liner. The initial pressure was built up with hydrogen or nitrogen. The catalyst used amounted to 10% by weight of the aldehyde charged. The average run took one hour.

Aldehydes.—Propionaldehyde, Eastman Kodak Co., b. p. 49.5°, n^{20}_D 1.3636; *n*-butyraldehyde, Eastman Kodak Co., b. p. 75–76°, n^{20}_D 1.3843; *n*-amyl aldehyde was prepared by the dehydrogenation of *n*-amyl alcohol over a copper catalyst at 300°, b. p. 102–3°; *n*-hexaldehyde was prepared by the dehydrogenation of *n*-hexyl alcohol over a copper catalyst at 300°, b. p. 129–131°.

Catalyst.—The chromium oxide used was prepared by the precipitation of chromium hydroxide from a cold 1 *N* solution of chromium nitrate by 1 *N* sodium hydroxide solution. This chromium hydroxide was dissolved in an excess of sodium hydroxide. The chromite solution, on standing overnight, gave a fine precipitated gel. The precipitate was washed anion free, dried at 100°, and screened to 8–10 mesh. It was then heated in an atmosphere of hydrogen at slowly increased temperatures up to 500°.

The aluminum oxide was prepared by precipitation of aluminum hydroxide from a cold 1 *N* solution of aluminum nitrate by 1 *N* sodium hydroxide solution. A sodium aluminate solution was formed by the addition of excess sodium hydroxide. The aluminum hydroxide was reprecipitated in the form of a gel by the addition of an ammonium chloride solution. The precipitate was washed anion free, dried at 110° and screened to 8–10 mesh. It was then heated in a stream of nitrogen to 350°.

The chromium oxide–nickel catalyst was merely a mixture of a nickel catalyst prepared by precipitation and a pure chromium oxide catalyst prepared as explained above.

Analysis of Products.—All distillations were carried out using a 36 in. Super-cal Heli Grid Podbielniak column. The unsaturated hydrocarbons were identified by boiling points, indices of refraction and carbon–hydrogen analysis. They were also hydrogenated to the saturated hydrocarbons which were identified in a similar manner. All aldehydes were identified by preparation of the corresponding 2,4-dinitrophenylhydrazones. The gaseous products were analysed by the Göckel method.[3]

The experimental results are represented in the table.

Summary

1. Normal aliphatic aldehydes were subjected to the action of chromium oxide catalysts at 385–410° and super-atmospheric pressures. Under these conditions a condensation followed by a dehydration and loss of carbon monoxide takes place with the formation of olefin hydrocarbons containing $(2n - 1)$ carbon atoms.

2. Propionaldehyde, *n*-butyraldehyde, *n*-amyl aldehyde and *n*-hexaldehyde were studied. The corresponding olefins were produced, namely, pentene-2, heptene-3, nonene-4, and undecene-5.

3. At lower temperatures (330°) the reaction goes mainly toward the formation of the unsaturated aldehyde. The unsaturated aldehydes were hydrogenated when the reaction was carried out in the presence of hydrogen, resulting in the formation of saturated aldehydes.

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(3) "U. O. P. Laboratory Test Methods for Petroleum and Its Products," Universal Oil Products Company, Chicago, 1937, p. 162.