[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Reaction of Propane with Carbon Monoxide in the Presence of Aluminum Chloride

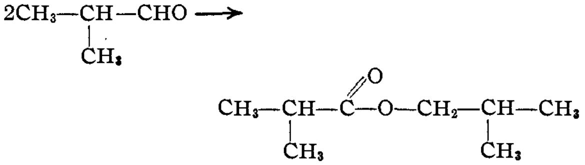
BY HERMAN PINES AND V. N. IPATIEFF

Butanes and pentanes react with carbon monoxide in the presence of aluminum chloride[1] to form a mixture of ketones and acids. The main product that resulted from the interaction of carbon monoxide and *n*-butane was methyl isopropyl ketone; smaller amounts of *n*-butyl *i*-butyl ketone and α-methylbutyric acid were also formed. Since *n*-butane under conditions of reaction might well have undergone isomerization to isobutane, it was thought that the presence of a tertiary carbon atom was required for the reaction to proceed. In order to test this hypothesis, the reaction of carbon monoxide with propane[2] was studied. It was found that propane reacted with carbon monoxide in the presence of aluminum chloride–hydrogen chloride when heated at 80° under an initial carbon monoxide pressure of 125 atmospheres.

The reaction product was decomposed with water. The upper layer, which consisted of organic material, was separated and steam distilled. The distillate contained isobutyric acid, isobutyl isobutyrate and 2,5-dimethyl-4-hexen-3-one; the respective yields of these compounds, based on carbon monoxide reacted were 5, 44 and 23 mole per cent. A mixture of unidentified higher boiling condensation products also was formed.

A similar reaction, when carried out in the absence of hydrogen chloride, proceeded more slowly. One mole of propane entered into reaction per 0.77 mole of carbon monoxide and 0.80 mole of aluminum chloride; the latter formed complexes with the products of the reaction.

The formation of the various compounds can be explained readily if it is assumed that isobutyraldehyde was the primary product of reaction of propane and carbon monoxide. Isobutyraldehyde, by means of intermolecular oxidation and reduction, can yield isobutyl isobutyrate

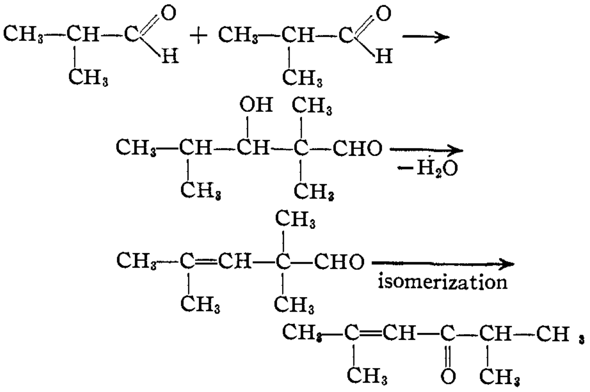


$$2CH_3-\underset{\substack{|\\CH_3}}{CH}-CHO \longrightarrow CH_3-\underset{\substack{|\\CH_3}}{CH}-\overset{\substack{O\\/\!/}}{C}-O-CH_2-\underset{\substack{|\\CH_3}}{CH}-CH_3$$

Isobutyric acid was separated from the steam distillate by the usual procedure, as described in the experimental part, and identified by means of its physical constants and solid derivatives.

The structure of 2,5-dimethyl-4-hexen-3-one was established by synthesis of the saturated ketone and confirmed by Raman spectral analysis (of which the original data have since been lost) on the saturated hydrocarbons obtained by complete reduction.

The formation of 2,5-dimethyl-4-hexen-3-one can be explained by the aldol condensation of isobutyraldehyde.

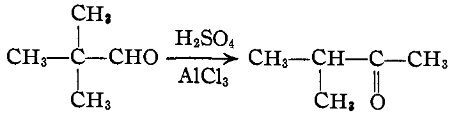


$$CH_3-\underset{\substack{|\\CH_3}}{CH}-C\Big\langle{}^{O}_{H} + CH_3-\underset{\substack{|\\CH_3}}{CH}-C\Big\langle{}^{O}_{H} \longrightarrow$$

$$CH_3-\underset{\substack{|\\CH_3}}{CH}-\overset{\substack{OH\\|}}{CH}-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-CHO \xrightarrow[-H_2O]{}$$

$$CH_3-\underset{\substack{|\\CH_3}}{C}=CH-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-CHO \xrightarrow[\text{isomerization}]{} CH_3-\underset{\substack{|\\CH_3}}{C}=CH-\underset{\substack{\|\\O}}{C}-\underset{\substack{|\\CH_3}}{CH}-CH_3$$

The isomerization of an aldehyde of the type of 2,2,4-trimethyl-3-penten-1-al to a ketone by the use of sulfuric acid[3] and aluminum chloride[1b] as catalysts has been reported. Thus 2,2-dimethylpropanal (pivalic aldehyde) yielded methyl isopropyl ketone.



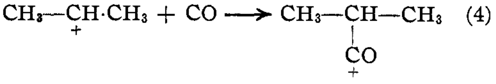
$$CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-CHO \xrightarrow[AlCl_3]{H_2SO_4} CH_3-\underset{\substack{|\\CH_3}}{CH}-\underset{\substack{\|\\O}}{C}-CH_3$$

The formation of isobutyraldehyde from the interaction of propane with carbon monoxide proceeded probably in the presence of catalysts through a chain mechanism as explained by the following series of steps.

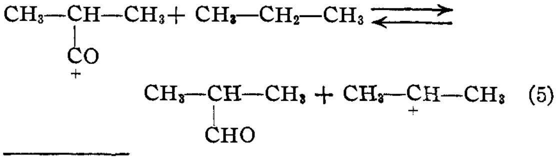
$$HCl + CO \rightleftarrows HCOCl \qquad (1)$$

$$HCOCl + AlCl_3 \rightleftarrows HCOAlCl_4 \rightleftarrows \overset{+}{H}\overset{+}{C}O(AlCl_4)^- \qquad (2)$$

$$CH_3-CH_2-CH_3 + H\overset{+}{C}O(AlCl_4)^- \rightleftarrows CH_3-\underset{+}{CH}-CH_3 + HCHO + (AlCl_4)^- \qquad (3)$$



$$CH_3-\underset{+}{CH}\cdot CH_3 + CO \longrightarrow CH_3-\underset{\substack{|\\CO\\+}}{CH}-CH_3 \qquad (4)$$



$$CH_3-\underset{\substack{|\\CO\\+}}{CH}-CH_3 + CH_3-CH_2-CH_3 \rightleftarrows CH_3-\underset{\substack{|\\CHO}}{CH}-CH_3 + CH_3-\underset{+}{CH}-CH_3 \qquad (5)$$

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(1) (a) H. Hopff, *Ber.*, **64**, 2739 (1931); **65**, 482 (1932); (b) H. Hopff, C. D. Nenitzescu, D. A. Isacescu and I. P. Cantuniari, *ibid.*, **69B**, 2244 (1936).

(2) H. Pines and V. N. Ipatieff (to Universal Oil Products Company, U. S. Patent 2,346,701 (April 18, 1944).

(3) S. Danilow and E. Venus-Danilowa, *Ber.*, **59B**, 377 (1926).

The chain initiation reaction as represented by equation 3 proceeds probably through a hydrogen exchange reaction similar to the one described by Bartlett, Condon and Schneider.[4]

Experimental Part

Materials.—C. P. grade of propane, obtained from Phillips Petroleum Company, was used.

Hydrogen chloride was prepared by the action of sulfuric acid on sodium chloride solution. The anhydrous hydrogen chloride prepared was stored in a steel pressure charger.

Carbon monoxide was prepared by the action of phosphoric acid on formic acid according to the method described by Thompson.[5]

Aluminum Chloride.—A resublimed grade of aluminum chloride obtained from Givaudan–Delawanna was used.

Reaction of Carbon Monoxide with Propane.—An electrically heated, rotating autoclave of a 3300-ml. capacity was charged with 600 g. (13.7 moles) of propane, 1200 g. (9.0 moles) of aluminum chloride, 140 g. (3.8 moles) of hydrogen chloride and with carbon monoxide to a pressure of 125 atmospheres. The autoclave was heated at 80°. When the pressure dropped to 80 atmospheres the bomb was recharged with carbon monoxide to 125 atmospheres. This procedure was repeated four times. After twelve hours of heating, the pressure remained constant.

The autoclave was then cooled and the gaseous products were released through (a) a soda-lime filled tower in order to remove hydrogen chloride; (b) a gas trap cooled to −78° by means of a solid carbon dioxide–acetone mixture in order to collect condensable gases, such as unreacted propane; (c) the non-condensable gases were passed through a wet test meter. A representative sample of the non-condensable gases was collected for analysis.

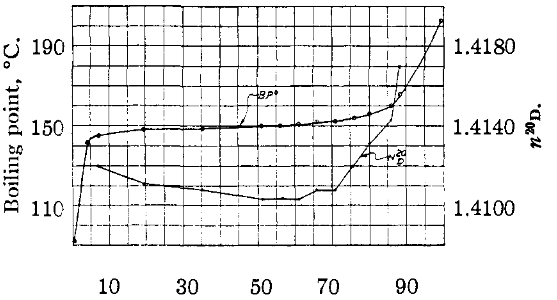

Fig. 1.—Distillation and index of refraction of the neutral products.

The bomb contained, after reaction, a viscous brown liquid which was decomposed by pouring it onto crushed ice.

On the basis of the pressure drop and the analysis of the gaseous products, it was calculated that 497 g. (11.3 moles) of propane, 1200 g. (9.0 moles) of aluminum chloride and 245 g. (8.7) moles of carbon monoxide entered into reaction.

The aluminum chloride complex reaction product yielded, after hydrolysis, 600 g. of organic material of which 400 g. was steam distilled.

The distillate, which contained organic acids, was neutralized with aqueous 25% solution of sodium hydroxide. The aqueous solution was then extracted with ether thus separating the neutral product from the organic acids now in the form of sodium salts.

Acidic Product.—The aqueous solution was heated on a steam-bath until its volume amounted to 150 cc. The concentrate was then acidified with hydrochloric acid and extracted with ether, dried with anhydrous sodium sulfate and distilled. After the removal of the ether, 41 g. of acid was obtained, which was distilled at atmospheric pressure. About 80% of the product distilled at 152–156°, $n^{20}\text{D}$ 1.3940, corresponding to isobutyric acid. On reaction with *p*-bromophenacyl bromide, it formed a solid derivative which melted at 78° and which did not show any depression in melting point when mixed with a similar derivative prepared from isobutyric acid.

Neutral Products.—The ether extract of the steam distillate after the removal of organic acid was redistilled on a column of a 10-plate efficiency. The results obtained are represented in Fig. 1.

Investigation of 35%–60% Cut.—B. p. 150°, $n^{20}\text{D}$ 1.4103.

Anal.[6] Calcd. for $C_8H_{14}O$ (octenone): C, 76.12; H, 11.19. Calcd. for $C_8H_{16}O_2$ (isobutyl isobutyrate): C, 66.66; H, 11.11. Found: C, 70.71; H, 11.68; d^{20}_4 0.8419; mol. wt., 132.

The product did not react with ammoniacal silver oxide, indicating the absence of aldehydes; the product reacted, however, with a dilute potassium permanganate solution indicating the presence of an olefinic double bond.

Semicarbazone.—One ml. of product was used for preparing this derivative. The semicarbazone crystals contained some oily material, indicating other compounds besides ketone. The semicarbazone melted at 125–127°. After three crystallizations from dilute ethanol the melting point rose to 129–130°.

Anal. Calcd. for $C_9H_{17}ON_3$ (semicarbazone of an octenone): C, 59.02; H, 9.29; N, 22.95. Found: C, 59.06; H, 9.71; N, 22.45.

Selective Hydrogenation.—Forty-one grams of the product was hydrogenated in a 450-cc. capacity rotating autoclave at 70° and in the presence of six grams of a nickel–kieselguhr catalyst and of hydrogen at 100 atmospheres pressure, measured at 25°. From the pressure drop, it was calculated that 0.66 mole of hydrogen was absorbed per one mole of compound submitted to hydrogenation. The material after hydrogenation was stable toward a dilute solution of potassium permanganate; it distilled at 148–150°, $n^{20}\text{D}$ 1.4080.

The **semicarbazone** of the hydrogenated product melted without decomposition at 145°. *Anal.* Calcd. for $C_9H_{19}ON_3$: C, 58.37; H, 10.27; N, 22.70. Found: C, 59.07; H, 9.92; N, 22.68.

This semicarbazone showed no depression of melting point when mixed with the semicarbazone of a known sample of 2,5-dimethyl-3-hexanone.

Synthesis of 2,5-Dimethyl-3-hexanone

The 2,5-dimethyl-3-hexanone was prepared by the oxidation of the corresponding alcohol.

The 2,5-dimethyl-3-hexanol was synthesized by treating isobutyraldehyde with isobutylmagnesium chloride according to standard procedures. The 2,5-dimethyl-3-hexanol distilled at 70° (29 mm.), $n^{20}\text{D}$ 1.4243.

Five ml. of the alcohol was dissolved in 25 ml. of glacial acetic acid. This solution was added gradually to a solution containing 5 g. of chromium oxide, 5 ml. of water and 50 ml. of glacial acetic acid. The mixture after being allowed to stand at room temperature for 16 hours was diluted with 50 ml. of water and 75% of it was allowed to distil. The distillate was neutralized with 25% aqueous sodium hydroxide and extracted thrice with 35-ml. portions of ethyl ether. The ether layer was washed once with water, dried over sodium sulfate and distilled. The obtained 2,5-dimethyl-3-hexanone boiled at 67° (48 mm.), $n^{20}\text{D}$ 1.4049.

The semicarbazone of this ketone melted without decomposition at 144°.

Hydrogenolysis.—The product obtained from selective hydrogenation was further hydrogenated at 165° in the presence of a nickel–kieselguhr catalyst at 100 atmos-

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[4] P. D. Bartlett, F. E. Condon and A. Schneider, THIS JOURNAL, 66, 1531 (1944).

[5] J. G. Thompson, *Ind. Eng. Chem.*, 21, 389 (1929).

[6] Analyses were made by Dr. T. S. Ma, University of Chicago.

pheres hydrogen measured at 25°; 0.66 mole of hydrogen was absorbed per 1 mole of product charged. Part of the ketone was transformed into the corresponding hydrocarbons. About 50% of the product distilled at 108–120°; $n^{20}\text{D}$ 1.3940. After redistillation over sodium to remove any alcohols present, a hydrocarbon was obtained that boiled at 108–109°, $n^{20}\text{D}$ 1.3941, d^{20}_4 0.6968.

Anal. Calcd. for C_8H_{18}: C, 84.18; H, 15.82. Found: C, 84.27; H, 15.55.

The structure of the hydrocarbon was corroborated by means of Raman spectral analysis[7] as 2,5-dimethylhexane.

Saponification.—Six grams of the same fraction of the neutral, steam-distilled product, boiling at 150°, was refluxed with alcoholic potassium hydroxide. The excess of potassium hydroxide was neutralized with hydrochloric acid. The solution was evaporated to dryness under reduced pressure. The solid was dissolved in 8 ml. of water; to this were added 10 ml. of ethanol and 0.75 g. of *p*-bromophenacyl bromide. The solution was refluxed for one hour, cooled, filtered and crystallized twice from 50% ethanol. The crystallized product melted at 76.5–77°. It showed no depression in melting point with a similar derivative prepared from a known sample of isobutyric acid.

In order to identify the alcoholic part of the ester, ten grams of the same fraction was heated in a sealed tube at 135° for four hours with 10 ml. of 25% aqueous potassium hydroxide. The aqueous layer was separated and distilled and the distillate was salted out with potassium carbonate; an upper layer was separated out which corresponded to isobutyl alcohol. On reaction with 3,5-dinitrobenzoyl chloride, a solid that melted at 85.5° was obtained which did not show any depression in melting point when mixed with a known sample of 3,5-dinitrobenzoate of isobutyl alcohol.

Acknowledgment.—The authors wish to thank Mr. R. C. Olberg for the valuable assistance rendered in connection with this work.

Summary

The condensation of propane with carbon monoxide in the presence of aluminum chloride and hydrogen chloride was described.

The products obtained from this reaction consisted of isobutyric acid, isobutyl isobutyrate and 2,5-dimethyl-4-hexen-3-one; the respective yields of these compounds, based on carbon monoxide reacted, were 5, 44 and 23 mole per cent.

A mechanism of reaction is suggested.

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[7] The Raman spectral analysis was made by Dr. E. J. Rosenbaum, University of Chicago.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Addition of Hydrogen Chloride to Isobutylene[1]

BY FRANK R. MAYO[2a] AND JOSEPH J. KATZ[2b]

The normal (Markovnikov) addition of halogen acids to alkenes is commonly supposed to proceed through the addition of a proton to the alkene to give a carbonium ion,[3] while the abnormal addition of hydrogen bromide proceeds through a free-radical chain mechanism.[4] The normal addition to isobutylene gives the *t*-butyl halide while the abnormal addition yields isobutyl bromide. While the carbonium ion mechanism is generally accepted in ionizing solvents, formation of free carbonium ions in non-ionizing solvents is doubtful. The addition of hydrogen chloride to isobutylene was therefore undertaken to throw some light on the mechanism of this reaction in particular, and of reactions of polar molecules in non-ionizing solvents in general. This work was interrupted by the War and there is little chance that it can be resumed in the near future. This paper therefore does not represent a completed research.

Previous Work.—The failure to observe homogeneous vapor-phase additions of halogen acids to alkenes (which additions should be simple and non-ionic) has been accounted for by Kistiakowsky and Stauffer.[5] They showed that the activation energies for the addition of hydrogen chloride and hydrogen bromide to isobutylene (29 and 23 kcal./mole, respectively) are high (resulting in very low rates at moderate temperatures), that the equilibria for the additions are unfavorable at high temperatures, but that the kinetics of the (presumably) bimolecular addition reaction are in no way abnormal. On the other hand, a dry, liquid mixture of isobutylene and hydrogen chloride reacts instantaneously[6d] at 0°, within one minute at −78°. Propylene and the butenes react slower. As pointed out by Kistiakowsky and Stauffer, the rapid liquid phase reactions must proceed by a mechanism very different from that in the gas reactions.

Maass and his associates[6] have been the principal contributors to our knowledge of these liquid-phase reactions. They studied the addition of hydrogen chloride to propylene in sealed glass bulbs, in the absence of water and solvents. Such

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[1] This paper is based on the Ph. D. dissertation of J. J. Katz, June, 1942. A preliminary account of this work was presented to the Division of Organic Chemistry at the St. Louis Meeting of the American Chemical Society, April 9, 1941, a more detailed account at the Atlantic City Meeting, April 10, 1946.

[2] Present addresses: (a) General Laboratories, United States Rubber Company, Passaic, N. J.; (b) Argonne National Laboratory, Chicago, Illinois.

[3] Kharasch and Reinmuth, *J. Chem. Ed.*, **8**, 1703 (1931). Robinson, "Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions," The Institute of Chemistry of Great Britain and Ireland, London, 1932. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 375.

[4] Mayo and Walling, *Chem. Rev.*, **27**, 351 (1940); Vaughn, Rust and Evans, *J. Org. Chem.*, **7**, 477 (1942).

[5] Kistiakowsky and Stauffer, THIS JOURNAL, **59**, 165 (1937).

[6] (a) Maass and Wright, *ibid.*, **46**, 2664 (1924); (b) Maass and Sivertz, *ibid.*, **47**, 2883 (1925); (c) Coffin, Sutherland and Maass, *Can. J. Research*, **2**, 267 (1930); (d) Coffin and Maass, *ibid.*, **3**, 526 (1930); (e) Holder and Maass, *ibid.*, **16B**, 453 (1938); (f) A. G. Brown, Master's Thesis, McGill University (1938).