In the case of the two small vessels, the hydrogen fluoride was poured from a small copper transfer vessel. At first the larger autoclave was filled by distillation of the hydrogen fluoride from a commercial cylinder. Later a blow case of about ten pounds capacity and operating under a few pounds of air pressure was used to blow the hydrogen fluoride into the reactor, thus eliminating the necessity for cooling.

Since both chloral and hydrogen fluoride are highly hygroscopic, it is essential that exposure to atmospheric moisture be kept to a minimum.

After the reaction mixture was heated for the specified time, the hydrogen fluoride was vented while the vessel and contents were still warm. Then water was added and the mixture poured from the reaction vessel and washed with water. In most of the experiments, the product solidified on cooling. The addition of a solvent such as chloroform or methylene chloride was desirable to facilitate further handling. The solution was washed with water and dilute potassium bicarbonate until free of hydrogen fluoride, dried over anhydrous sodium sulfate and the solvent evaporated. The residual material was further heated under vacuum on a steam-bath until essentially constant weight was reached. This crude product on cooling varied from a brown, viscous oil to a cream-colored solid. In several cases, noted in Table I, the washed product was stripped of volatile material by a steam distillation.

In the exploratory runs in the smaller vessels, this crude product was generally not investigated further.

The crude product from the larger runs solidified on cooling, but was generally low melting. In order to get an estimate of the DDT and oily by-products present, a simple refinement procedure was adopted. The crude molten product was poured rapidly into an approximately equal weight of methanol. A homogeneous solution was formed for a short time but DDT crystallized rapidly, and, after being cooled to 20°, the solid was filtered and air dried. The mother liquor was then freed of solvent leaving an oily residue.

Acknowledgment.—We are indebted to Mr. A. Struck for the spectrophotometric determination and to Messrs. F. J. Frere, I. D. Carter and J. R. Newsome for the analytical data.

Summary

Chloral and chlorobenzene have been condensed in the presence of hydrogen fluoride to give good yields of DDT. Copper and stainless steel equipment were used successfully with slight corrosion in the latter case. Results in a black iron vessel were less favorable. The use of chloral hydrate and chloral alcoholate in place of chloral has been investigated to a limited extent.

STAMFORD, CONN. RECEIVED MAY 4, 1946

[CONTRIBUTION FROM THE GULF RESEARCH & DEVELOPMENT CO.]

Catalytic Synthesis of Hydrocarbons and Oxygenated Compounds from Ketene and its Relation to the Fischer–Tropsch Synthesis

BY B. R. WARNER, M. J. DERRIG AND C. W. MONTGOMERY

It was early proposed by Fischer and Tropsch[1] that the catalytic synthesis of hydrocarbons from hydrogen and carbon monoxide proceeds through the polymerization of methylene radicals, the latter being formed by the reduction of metallic carbide produced from the metal and carbon monoxide. Craxford and Rideal[2] in a later investigation also postulated the formation and utilization of carbides in the Fischer–Tropsch reaction. As Bahr and Jessen[3] showed, precipitated and reduced cobalt reacts with carbon monoxide at 230° to yield the carbide, Co_2C. While these carbides are reduced in acid solution to give gaseous, liquid and solid hydrocarbons,[4] the reaction with hydrogen yields methane almost exclusively.[3]

It is perhaps significant that in the Fischer–Tropsch synthesis oxygenated compounds are generally produced along with the hydrocarbons[4] even at low pressures. It is possible that oxygenated compounds either are actual intermediates in the synthesis or are produced in side reactions. That the formation of oxygen-containing compounds is an intermediate step in the formation of hydrocarbons was first suggested by Elvins and Nash.[5] The possibility that acetone is an intermediate was investigated by Smith[6] but the hydrocarbons obtained with acetone, and acetone and hydrogen, over a cobalt–copper–mangenese oxide catalyst, were different in character from those usually obtained from hydrogen and carbon monoxide. Recently Eidus[7] investigated the reactions of methyl alcohol, ethyl alcohol and formic acid on a cobalt–thoria–kieselguhr catalyst with the view that these compounds might be intermediates. Although hydrocarbons were obtained, the conclusion reached was that these were formed from the secondary reaction between hydrogen and carbon monoxide, the primary reaction being the decomposition of the alcohols and formic acid into hydrogen and carbon monoxide. With the use of Balandin's multiplet theory of catalysis,[8] Eidus postulates the intermediate formation of methylene radicals without assuming the intermediate formation of carbide.

A direct test of the methylene theory would be to supply the catalyst with methylene radicals. It was thought that ketene might possibly func-

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(1) Fischer and Tropsch, *Ber.*, **59**, 830 (1926).

(2) Craxford and Rideal, *J. Chem. Soc.*, 1604 (1939).

(3) Bahr and Jessen, *Ber.*, **63**, 2226 (1930).

(4) Fischer and Tropsch, *Brennstoff-Chem.*, **9**, 21 (1928).

(5) Elvins and Nash, *Nature*, **118**, 154 (1926).

(6) Smith, Hawk and Golden, THIS JOURNAL, **52**, 3331 (1930).

(7) Eidus, *Bull. acad. sci. U. R. S. S.*, 65–72 (1943); *Natl. Petroleum News*, **37**, No. 14, R 302, 6 (1945).

(8) Balandin, *J. Russ. Phys.-Chem. Soc.*, **61**, 909 (1929); *Acta Physicochim. U. R. S. S.*, **2**, 177 (1935).

tion as a source of methylene radicals and that it also might act as an intermediate in the synthesis. Methylene radicals have been obtained by the photolysis of ketene and have been shown to yield hydrocarbons higher than methane.[9] Thermal production of methylene radicals from ketene was attempted by Williamson,[10] who obtained as final products carbon monoxide, methane and carbon, presumably through the reactions, $CH_2CO \rightarrow CH_2 + CO$ followed by $CH_2 + CH_2 \rightarrow CH_4 + C$. Pearson[9(c)] identified methylene radicals from the thermal decomposition of ketene by means of the mirror method.

In the Fischer–Tropsch synthesis, methylene radicals on the catalyst surface would be surrounded largely by adsorbed carbon monoxide (adsorbed hydrogen being small[2]). The fact that methylene and carbon monoxide can combine to form ketene in detectable quantities[11] also indicates the possibility that ketene may form and may be intermediate in the Fischer–Tropsch synthesis.

These facts made it a matter of interest to determine whether ketene decomposes catalytically into methylene and carbon monoxide, and whether these react further to give products similar to those obtained from hydrogen and carbon monoxide.

Experimental

Ketene was prepared in good yields by the depolymerization of diketene[12,13] and purified by distilling from a trap at −78° into a trap at liquid nitrogen temperature. After pumping off non-condensable and low-boiling materials, the ketene was distilled into a bulb with an inlet tube extending to its bottom, the outlet being connected to the catalyst by means of a stop-cock. The catalyst consisted of 50 g. of fresh cobalt–thoria–kieselguhr pellets and was reduced with hydrogen at 400° before use. A mixture of ketene vapor and hydrogen was passed over the catalyst at 200° by bubbling hydrogen through liquid ketene kept at −60°. The catalyst temperature rose immediately and was held at 210°. The products were fractionated by passing them through a water condenser and traps held at Dry Ice–acetone and liquid nitrogen temperatures. Gaseous products were measured by means of a wet test gas meter. Unreacted ketene was absorbed in 20% potassium hydroxide solution.

Results

In a typical experiment the following results were obtained, charge, 7.35 liters of hydrogen and 20 cc. of liquid ketene (−60°). Assuming the density of liquid ketene to be about 0.8, the charge of ketene weighed approximately 16 g. Because of the uncertainty in the density of ketene at −60°, weight balances were based on the amount of carbon monoxide formed and the amount of oxygen in the products. The liquid condensable at 25° analyzed for 81.9% C, 14.4% H and 3.7% O; Dry Ice condensate analyzed for 79.5% C, 15.4% H and 5.1% O. The total oxygen in these products therefore corresponds to 0.45 g. ketene. Carbon monoxide (8.82 g.) was found in the gaseous product and this amount is equivalent to 13.30 g. ketene, making a total of 13.75 g. of ketene reacting. The following weight balance was obtained:

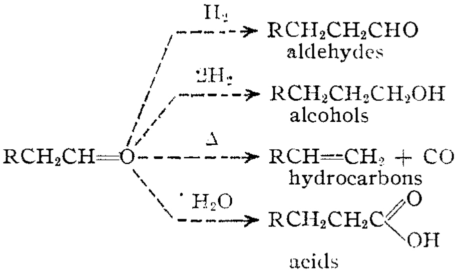
Product	Weight, g.	Wt. % yield (13.75 g. ketene reacting)
Methane	0.38	2.76
Ethylene	.37	2.69
Propylene	.52	3.78
Total liquid	3.00	21.82
Wax	0.50	3.64
Carbon monoxide	8.82	64.15
Total	13.59	98.84

The gaseous products were identified by separation into C_1, C_2, C_3 and C_4 fractions in a Podbielniak distillation column and the unsaturation determined by bromination. The liquid product was largely of a gasoline nature as indicated by its boiling range and carbon and hydrogen content. The small amount of waxy product was not identified as individual compounds, since as in the Fischer–Tropsch process, the wax appeared to consist of a complex mixture of compounds. Its softening point (30–35°) and analysis (79.2% C, 15.6% H and 5.2% O) approximate a wax obtained by the synthesis from hydrogen and carbon monoxide. A reasonable assumption to explain the experimental results involves preliminary catalytic decomposition of ketene.

$$CH_2CO \longrightarrow CH_2 + CO$$

followed by polymerization of methylene, $nCH_2 \rightarrow (CH_2)_n$, or by reactions such as $nCH_2 + CH_2CO \rightarrow CH_3(CH_2)_{n-1}-CH{=}C{=}O$, and $CH_3(CH_2)_{n-1}-CH{=}C{=}O \rightarrow CH_3(CH_2)_{n-2}-CH{=}CH_2 + CO$.

The latter reactions involving higher ketenes are favored since they could account for the presence of oxygenated compounds in the Fischer–Tropsch synthesis as follows



Formation of ketenes would be favored at high pressures where the CO concentration on the catalyst would be high. Thus the hydrogenation of carbon monoxide at 100 atmospheres and 400°

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[9] (a) Norrish, Crone and Saltmarsh, *J. Chem. Soc.*, 1533 (1933); THIS JOURNAL, **56**, 1644 (1934); (b) Ross and Kistiakowsky, *ibid.*, **56**, 1112 (1934); (c) Pearson, Purcell and Saigh, *J. Chem. Soc.*, 409 (1938); (d) Barrow, Pearson and Purcell, *Trans. Faraday Soc.*, **35**, 880 (1939); (e) Rosenblum, THIS JOURNAL, **63**, 3322 (1941).

[10] Williamson, THIS JOURNAL, **56**, 2216 (1934).

[11] (a) Staudinger and Kupfer, *Ber.*, **45**, 501 (1912); (b) Rice and Glazebrook, THIS JOURNAL, **56**, 741 (1934).

[12] Boese, *Ind. Eng. Chem.*, **32**, 16 (1940).

[13] Obtained through the courtesy of the Carbide and Carbon Chemicals Corp.

yielded mixtures of oxygen compounds containing alcohols, aldehydes, ketones and acids.[14]

Assuming that the formation of hydrocarbons from ketene proceeded step-wise in the following manner

(a) $CH_2CO \longrightarrow CH_2 + CO$

(b) $CH_2 + CH_2CO \longrightarrow CH_3CH{=}C{=}O$

(c) $CH_3CH{=}C{=}O \longrightarrow CH_2{=}CH_2 + CO$

(d) $CH_2 + CH_3CH{=}C{=}O \longrightarrow$
$CH_3CH_2CH{=}C{=}O \longrightarrow CH_3CH{=}CH_2 + CO$, etc.

a reaction mechanism for the Fischer–Tropsch synthesis may be formulated from the above reactions by providing a source of methylene radicals. Such a source might be the usual one from metal carbide and hydrogen or that postulated by Eidus.[7]

Summary

Ketene in the presence of hydrogen reacts on a Co–ThO_2–kieselguhr catalyst to yield hydrocarbons and oxygenated compounds which are similar to the products of the Fischer–Tropsch synthesis. The possibility that ketene is an intermediate in the Fischer–Tropsch synthesis is discussed.

PITTSBURGH, PA. RECEIVED MARCH 25, 1946

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(14) Fischer and Tropsch, *J. Inst. Fuel*, **10**, 10 (1936).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Studies in Organic Peroxides. XII. Molecular Refractivity and the Structure of Organic Peroxides

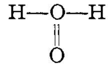
BY NICHOLAS A. MILAS, DOUGLAS M. SURGENOR[1] AND LLOYD H. PERRY[2]

Enough pure liquid organic peroxides have now been synthesized in this Laboratory and elsewhere to justify a study of the influence of molecular refraction on the structure of this class of organic compounds. The molecular refraction of pure hydrogen peroxide[3] and of water[4] have been determined very accurately. By simply subtracting the observed molecular refraction of water from that of hydrogen peroxide, a value of 2.19 is obtained, which represents the atomic refraction of the peroxidic oxygen (O*). This value has been used as the basis for the calculations of the molecular refractions of all of the liquid peroxides listed in Table I. By merely adding this value to the calculated molecular refraction of the oxygen analog (Column 6) of a given peroxide, a value is obtained which is compared with the observed molecular refraction (Column 2). A large deviation between the observed and the calculated molecular refraction would indicate an abnormality in the structure of the peroxide.

Rieche[5] has proposed two different values for the molecular refraction of the peroxide group (—O—O—): 4.04 for the dialkyl peroxides and 3.7 for the alkyl hydroperoxides. These values are somewhat inconvenient and much less useful than the single value adopted in the present investigation. Besides, by subtracting 1.643, the atomic refractivity of oxygen in ethers, from 4.04, and, similarly, 1.525, the atomic refractivity of oxygen in alcohols, from 3.70, values of 2.40 and 2.17 respectively are obtained which agree rather well with the atomic refractivity of the peroxidic oxygen.

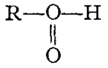
Discussion

The value of the atomic refractivity of the peroxidic oxygen is, within the limits of experimental error, almost identical with that of the carbonyl oxygen (2.211). It is therefore conceivable that hydrogen peroxide and the simple aliphatic alkyl hydroperoxides and dialkyl peroxides may have the unsymmetrical oxo-oxide structures (Ia, b, c) rather than the normal peroxide structures (IIa, b, c). The bulk of experimental evidence, however, is certainly not in favor of the oxo-oxide structure. For example, the dissociation of hydrogen peroxide under the influence of ultraviolet light into free hydroxyl radicals,[6] and the thermal decomposition of simple aliphatic peroxides are more in accord with the normal structures. This is particularly true in the case of ditertiary alkyl peroxides[e,f,g] in which the carbon–oxygen bond seems to be much stronger than the oxygen–oxygen bond. The extraordinary stability of these peroxides is probably due to this relationship.



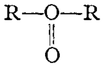
$$H\text{—}\overset{\overset{}{}}{\underset{\underset{\textstyle O}{\|}}{O}}\text{—}H$$

Ia



$$R\text{—}\underset{\underset{\textstyle O}{\|}}{O}\text{—}H$$

Ib



$$R\text{—}\underset{\underset{\textstyle O}{\|}}{O}\text{—}R$$

Ic

H—OO—H
IIa

R—OO—H
IIb

R—OO—R
IIc

With only a few exceptions, the small exaltations which exist in the simple aliphatic alkyl hydroperoxides, dialkyl peroxides and hydroxyalkyl peroxides are probably due to experimental

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[1] Present address: Harvard Medical School, Boston, Mass.

[2] Present address: Union Bay State Chemical Company, Cambridge, Mass.

[3] Maass and Hatcher, THIS JOURNAL, **42**, 2548 (1920).

[4] "Landolt-Börnstein Physikalisch-chemische Tabellen," nos. 182, 184, 5. Aufl., Berlin, 1926.

[5] Rieche, "Alkyl Peroxyde und Ozonide," Theodor Steinkoff, Dresden, 1931, pp. 98–100.

(6a) Urey, Dawsey and Rice, THIS JOURNAL, **51**, 1371 (1929); (b) Milas, Kurz and Anslow, *ibid.*, **59**, 543 (1937); (c) Davis and Ackerman, *ibid.*, **67**, 486 (1945).