[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

Oxidation Studies. II. The Oxidation of Diisobutylene in the Presence of Potassium Hydroxide at Elevated Temperature and Pressure

BY R. W. BOST AND L. B. LOCKHART, JR.[1]

Though one of the oldest known reactions of organic compounds is that of oxidation, very little investigation has been done on the oxidation of organic compounds by molecular oxygen at elevated temperatures and pressures. It is with the hope of filling this gap that this work was undertaken. This paper consists of a report of the action of molecular oxygen on diisobutylene in the presence of potassium hydroxide and at a temperature of 100° and a pressure of 100 lb. per sq. in.

Previous work[2,3] in this Laboratory has shown that molecular oxygen under the conditions described in this paper first yields peroxides, which may then undergo fission forming aldehydes and ketones. The aldehydes then may be further oxidized to the corresponding acids.

As far as the authors are aware, this is the first attempt to oxidize a simple unsaturated organic compound at elevated temperatures and pressures and to obtain quantitative data on the oxidation products.

Diisobutylene seemed to be an almost ideal substance to study. It is a typical unsaturated hydrocarbon; its vapor pressure and other physical properties lie within a desirable range; it may be obtained commercially since it is an intermediate in the production of isoöctane. Its chief disadvantage is the presence of isomers[4,5] leading to the formation of two sets of products.

The diisobutylene was obtained from the Standard Oil Development Company of New Jersey. It was purified by distillation through a five-foot vacuum-jacketed, silvered column packed with Fenske glass helices. The fraction distilling from 101.5–103.5° was collected (n^{20}_{D}, 1.4106). This was redistilled from metallic sodium through an 18-inch Widmer column and the fraction distilling in the range 101.5–102.5° was collected. It was free of peroxides and had an index of refraction of 1.4087 at 25°.

The oxygen was the regular grade (99.5%) obtained from the Air Reduction Company and was used without further treatment.

Apparatus.—The apparatus consisted essentially of three parts: a pressure bomb, a constant temperature bath and a pressure-recording gage. The bombs were made of high strength alloy steel and were cadmium plated to prevent corrosion. The pressure changes were followed by means of a Bristol pressure-recording gage connected to the bombs by high pressure tubing. The constant-temperature bath was an enclosed electrically heated steam-bath with a constant water-level device. Provision was also made for cooling the bombs without removing them from the bath.

Procedure.—One hundred milliliters of the hydrocarbon was placed in an 8-oz. bottle, 10 g. of Merck reagent potassium hydroxide added and then the bottle and contents placed in a bomb which had been previously calibrated. A 30-ml. beaker was inverted over the mouth of the bottle, the bomb securely closed and then charged with oxygen to 100 lb. per sq. in. pressure. This charge was flushed from the system through outlet valves and the process of flushing repeated twice. Finally the bombs were charged with oxygen to 100 lb. per sq. in., the valves to the bombs closed, the pressure-recording gage set, and the heating bath started.

The course of the reaction was followed by observing the pressure drop on the pressure-recording chart. The pressure increased as the temperature rose until a pressure of 125 lb. per sq. in. was reached at 100°. The pressure remained fairly constant over a period of forty-five to sixty minutes and then began to drop. The reaction had an induction period of ninety to one hundred and twenty minutes, considering the induction period to be that length of time required for the rate of change of pressure with time to change from zero to its maximum value. The reaction was considered to be complete when there was no further change in pressure, usually after eight hours. At this point the bomb was cooled, opened and the oxidation product examined. A total of two liters of diisobutylene was treated in this manner and the oxidation products combined.

TABLE I

OXIDATION DATA OF A TYPICAL RUN

Initial pressure	100 lb. per sq. in.
Final pressure	10 lb. per sq. in.
Maximum pressure	125 lb. per sq. in.
Induction period	90–120 minutes
Temperature	100°
Time of exposure	8 hours
Oxygen consumed (total for 20 runs)	48,960 cc. at 25° and 1 atm.. or 2.00 moles

Sufficient water to dissolve the potassium hydroxide and other solids was added and the resulting phases separated, washed and then analyzed. Qualitative tests showed the presence of methyl ketones, acids, alcohols, 1,2-glycols and traces of peroxides and aldehydes. The specific substances identified were acetone, 4,4-dimethylpentanone-2, formic acid, pivalic acid, formaldehyde and carbon dioxide.

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[1] Ethyl Dow Fellow in Chemistry.

[2] R. W. Bost, *Science*, **88**, 440 (1938).

[3] Leiserson, Master's Thesis, Univ. of N. C., June, 1940 (unpublished).

[4] McCubbin and Adkins, THIS JOURNAL, **52**, 2547 (1930).

[5] Whitmore, *et al., ibid.*, **54**, 3706 (1932).

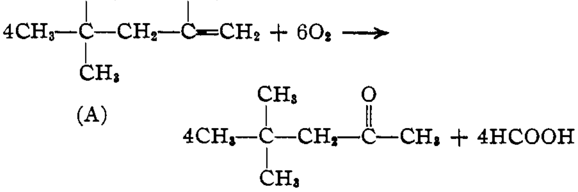
Quantitative determinations of the formic and pivalic acids were made using aliquot portions of the potassium hydroxide phase. The aliquot, after being strongly acidified with 85% phosphoric acid, was distilled to give a water solution of the volatile organic acids. The total acidity of the distillate was determined by titration with 0.1 *N* sodium hydroxide solution using phenolphthalein as indicator. Formic acid was determined gravimetrically by the mercuric chloride method.[6] The difference between the total acidity and the formic acid gave the amount of other volatile organic acids present and was regarded as pivalic acid. Titration of the distillate and also of the undistilled residue with potassium permanganate solution in basic medium showed the presence of other reducing agents. They were present in quantities too small to afford identification.

The diisobutylene phase was fractionated through a 12-inch Widmer column. Qualitative tests were run on all fractions. Aldehydes were determined by the use of Schiff reagent, methyl ketones by the iodoform reaction, peroxides by the thiocyanate method, alcohols by the reaction with metallic sodium and by the ceric nitrate test, 1,2-glycols by the periodic acid test, acids by the reaction with litmus and unsaturation by the reduction of neutral permanganate and by the reaction with bromine in a carbon tetrachloride solution. The presence of acetone was detected by the formation of a blue color with *o*-nitrobenzaldehyde in the presence of sodium hydroxide (Penzoldt's test). Formaldehyde was detected by the resorcinol test. The lower fractions were analyzed quantitatively for methyl ketones (acetone) by the iodoform method.[7] The higher ketones (in fractions having boiling points greater than 102°) were determined by the hydroxylamine method.[8] Where ketones occurred to any appreciable extent, attempts were made to obtain derivatives. The hydroxyl content of several fractions was also determined using the acetyl chloride–pyridine method.[9]

The diisobutylene phase was separated into definite fractions by distillation. Fraction 1 (b. p. 60–99.5°) gave positive tests for aldehydes, methyl ketones and unsaturation. The bulk of the acetone recovered was present in this fraction together with a considerable quantity of diisobutylene. Fractions 2–5 were mainly diisobutylene with only traces of aldehydes and methyl ketones. Fractions 6 and 7 (b. p. 105.5–131° and 131–137°) gave increasingly strong tests for methyl ketones. Alcohols and 1,2-glycols began to appear also. Analysis showed fraction 7 to contain the main portion of the 4,4-dimethylpentanone-2 but this amounted to only 17% of the fraction. Quantitative hydroxyl determinations showed hydroxyl compounds to be present in negligible amounts. The higher fractions gave stronger tests for 1,2-glycols, alcohols and acids (probably formed by decomposition of the peroxide during distillation). All fractions gave tests for unsaturation. The refractive indices increased from a value of 1.4040 at 25° for fraction 1 to a value of 1.4431 at 25° for fraction 12. A residue of dark viscous tar was left (b. p. greater than 225° at atmospheric pressure). Analysis of this tar gave the following results: C, 78.16%; H, 11.19%; O, 10.65% which corresponded to a C:H:O ratio of 9.8:16.8:1.00, or slightly less than one oxygen per hydrocarbon unit.

Acetone was characterized by formation of dibenzalacetone (m. p. 110–111°), 4,4-dimethylpentanone-2 by its semicarbazone (m. p. 176°), and formic acid by its *p*-bromphenacyl ester (m. p. 136–7°). 2,4-Dinitrophenylhydrazones were prepared from other fractions of distillate but were neither obtainable in sufficient purity for analysis nor did they give sharp melting points.

Discussion of Results.—Theoretically the initial reaction between oxygen and diisobutylene should be the formation of a peroxide which would undergo fission to give an aldehyde and a ketone. Under the oxidizing conditions this aldehyde would be ultimately converted to the acid. Considering the two isomers of diisobutylene to be present in the ratio of four parts of (A) to one of (B) as shown by Whitmore and Church[10] and by McCubbin and Adkins[4] and assuming the ratio to have been unchanged by distillation or by the potassium hydroxide, the over-all reactions would be as follows



$$4CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\overset{CH_3}{C}=CH_2 + 6O_2 \longrightarrow 4CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 + 4HCOOH$$

(A)

TABLE II

PRODUCTS OBTAINED BY THE OXIDATION OF DIISOBUTYLENE IN THE PRESENCE OF POTASSIUM HYDROXIDE

Substance	Theoretical	Yield in moles, actual	Per cent.
Acetone	0.27	0.055	20.4
Pivalic acid	.27	.077	29.5
4,4-Dimethylpentanone-2	1.07	.070	6.5
Formic acid	1.07	.31	29.0
Carbon dioxide	..	.20	..

TABLE III

DISTRIBUTION OF OXYGEN AMONG PRODUCTS

Substance	Moles	% of orig. O_2 present
Acetone	0.055	1.4
4,4-Dimethylpentanone-2	.070	1.75
Other carbonyl compounds	.161	4.0
Formic acid	.31	15.5
Pivalic acid	.077	3.85
Carbon dioxide	.20	10.0
Residue or "Gum"	...	2.0
Total oxygen accounted for		38.5

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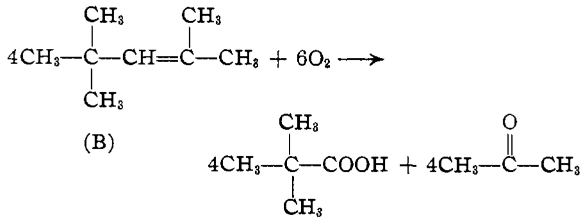
(6) Thorpe and Whiteley, "A Student's Manual of Organic Chemical Analysis," Longmans, Green and Company, Ltd., London, p. 173.

(7) Thorpe and Whiteley, *ibid*,, p. 192.

(8) Bryant and Smith, THIS JOURNAL, **57**, 57 (1935).

(9) Smith and Bryant, *ibid*., **57**, 61 (1935).

(10) Whitmore and Church, *ibid*., **54**, 3710 (1932).



(B)

$$4CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=\overset{CH_3}{C}-CH_3 + 6O_2 \longrightarrow 4CH_3-\underset{CH_3}{\overset{CH_3}{C}}-COOH + 4CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

The above assumption gives us a basis for calculating the yields of oxidation products. The low yield of the expected ketones as compared to the acids formed at the same time may be explained by the fact that the ketone is influenced by the potassium hydroxide for a much longer period of time than is the intermediate aldehyde. Under such conditions the primary reaction of the aldehydes is one of oxidation rather than condensation or polymerization. The ketones, however, remained in contact with the potassium hydroxide from the time of formation until the time of separation of the phases. There is evidence that secondary reactions took place giving rise to unpredicted compounds and substances present in quantities too small for absolute identification.

Summary

1. The action of molecular oxygen on diisobutylene in the presence of potassium hydroxide has been studied at 100° and 100 lb. per sq. in. pressure. The course of the reaction was followed by noting the drop in pressure in the bomb. Under the aforementioned conditions diisobutylene has an induction period of ninety to one hundred and twenty minutes. The reaction is essentially complete after eight hours.

2. A qualitative and quantitative study was made on the oxidation products.

3. The chief products obtained were acetone, 4,4-dimethyl pentanone-2, carbon dioxide, formic acid, and pivalic acid.

4. The presence of oxygen-containing compounds boiling higher than any of the predicted products was shown. These could not be obtained in sufficient quantity and purity for identification. Qualitative tests indicated that these substances contained the CH_3CO— and —OH groups.

CHAPEL HILL, N. C. RECEIVED MAY 19, 1941

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The Action of Elementary Fluorine upon Organic Compounds. XI. The Vapor Phase Fluorination of Benzene

BY NOBUKAZU FUKUHARA AND LUCIUS A. BIGELOW

In Paper X of this series[1] we have described an efficient apparatus for the vapor phase fluorination of volatile organic liquids over a heated copper gauze catalyst and its successful use for the fluorination of acetone. This work led us rather directly to undertake the more difficult problem of fluorinating benzene. In the past, neither benzene itself, nor aromatic compounds in general, have been caused to react with elementary fluorine with satisfactory results. Now, however, we have found that the hydrocarbon can be fluorinated without any difficulty in the apparatus just referred to, yielding a clean, though complex, product.

Experimental Procedure

The fluorinations were carried out essentially as described before,[1] except that the reactor had an initial temperature of about 90° and was swept out with nitrogen for roughly half an hour after each period of operation, in order to collect all of the product volatile at this temperature. In most cases, the gas volume ratio of $F:C_6H_6:N$ used was 4:1:2. Under our present operating conditions, it was not practicable to raise the fluorination ratio of $F:C_6H_6$ above 6:1 in any case, and therefore the fluorine was actually well diluted by the excess of benzene. Nevertheless, a series of runs was made, in which the dilution ratio of F:N was increased progressively, in order to determine the effect of this change upon the reaction.

TABLE I

THE EMPIRICAL CUTS OBTAINED BY FRACTIONATING FLUORINATED BENZENE

Liquid vol. % of material boiling at	Gas volume ratio of $F:C_6H_6:N$ 4:1:0	4:1:2	4:1:4	4:1:8	4:1:16
−128 to −105 (mostly CF_4)	25	10	10	15	20
−105 to −58 (mostly C_2F_6)	Trace	Trace	5	5	5
−58 to −5 (largely C_3F_8)	5	Trace	5	10	5
−5 to 40	..	10	10	5	10
40 to 79	..	15	10	5	5
Above 79	..	65	65	60	55
Total vol. of condensate per hr. in ml.	1.2	1.1	1.3	1.8	1.6

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[1] Fukuhara and Bigelow, THIS JOURNAL, 63, 788 (1941).