[CONTRIBUTION FROM THE UNIVERSITY OF BRUSSELS]

THE ACTION OF OXYGEN ON 1,4-DIMETHYLCYCLOHEXANE[1]

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In a note presented to the Bulletin of the Science Section of the Belgian Academy in February, 1926, one of us gave an account of qualitative observations made on the change which samples of dimethylcyclohexanes had undergone when kept in contact with the air for several years. We also made preliminary observations on the spontaneous oxidation of 1,3-dimethylcyclopentane. The latter phenomenon occurs at ordinary temperatures sufficiently rapidly to have been studied more closely and is described in a note appearing in the *Bulletin de la Société Chimique de Belgique.*[4]

Since then, thanks to grants from the American Petroleum Institute, we have been able to go more deeply into this study of the oxidation of different cyclohexane and cyclopentane hydrocarbons with side chains. This paper contains the observations made on one of them.

The 1,4-dimethylcyclohexane was prepared by the hydrogenation of very pure *p*-xylene (m. p. 13.10°). The saturated cyclic hydrocarbon so obtained is not a definite chemical individual, but a mixture of two stereoisomers, the relative proportions of which vary with the conditions of hydrogenation. The use of nickel catalysts at temperatures between 160 and 180° gave a product which distilled almost completely at 121.0–121.5° under a pressure of 750.6 mm. It is defined by d_4^0 0.7872, d_4^{15} 0.7746, and by a critical solution temperature in aniline of 50°. When platinum black at ordinary temperature is used as a catalyst, in an acetic acid medium, we obtain a saturated hydrocarbon distilling almost completely from 121.75 to 122.25° under a pressure of 733.8 mm. It is defined by d_4^0 0.7930, d_4^{15} 0.7804, and by a critical solution temperature in aniline of 48.5°. These constants are for products perfectly purified from all trace of residual xylene.

Spontaneous Oxidation at Room Temperature and in Diffused Light.—A 10-cc. sample of the hydrocarbon was enclosed in a cylindrical glass reservoir of 420-cc. capacity, which was connected with a mercury manometer and which communicated by means of tubes to stopcocks leading, respectively, to an exhaust pump and to a gasometer filled with oxygen. After chilling the reservoir in ice, it was exhausted and oxygen then allowed to enter, passing over dehydrating substances. The stopcocks are then separated by sealing off the tubes leading to them, and the apparatus is put in a place where it will

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[1] This paper contains some of the results obtained in an investigation on "Action of Oxygen and Air on Cyclopentane and Cyclohexane Hydrocarbons with Side Chains," listed as Project No. 2 of American Petroleum Institute research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by the Universal Oil Products Company. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

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[4] *Bull. soc. chim. Belg.*, **36**, 206 (1927).

not receive the direct rays of the sun. A movable cathetometer on a shaft graduated in millimeters with a vernier for tenths enables the operator to read the level of the manometer. Before each reading the reservoir is surrounded with ice. We are thus enabled to follow the diminution of the interior pressure as a function of time. The numerical results below show the absorption of oxygen by the hydrocarbon.

Sample	Date of reading	Pressure, mm. Hg	Press. decrease
Prepared from Ni	13-12-1926	666.3	..
	26- 9-1927	651.2	15.1
	9- 6-1928	636.6	29.7
Prepared from Pt	20-12-1926	666.8	..
	26- 9-1927	655.9	10.9
	9- 6-1928	648.8	18.0

The real values of the diminution of pressure of the oxygen are doubtless greater than the measured decrease, for the oxidation reaction actually produces other gases, as we shall see later.

The spontaneous oxidation of the hydrocarbon in diffused light thus shown is much less rapid than that observed by one of us under the same conditions with dimethyl-1,3-cyclopentane.[4] In the latter case we found a diminution in pressure of 528.5 mm. in 151 days.

The difference in the vapor pressures of the hydrocarbons at room temperature is inadequate, by far, to account for the enormous inequality of the velocities of autoxidation. Some constitutive influence is surely dominant.

After opening the apparatus, we detected peroxides in the liquid by employing potassium iodide and indigo carmine as reagents.

Spontaneous Oxidation at Room Temperature and in Sunlight.—Ten cc. of each sample was enclosed, with a known pressure of oxygen, in a larger flask of about two liters' capacity and having a narrow neck which was further reduced in dimensions by drawing down to a convenient size. To the bottom of each flask there was sealed a cylindrical vessel of about 20-cc. capacity. To the neck of the flask a narrow side tube was sealed, drawn down to capillary size and sealed off at its end. After placing the hydrocarbon in the cylindrical vessel, the system is cooled in ice, evacuated and then filled with dry oxygen at a known pressure, which is indicated by a manometer. Then the vessel is sealed at the neck. The flask is then inclined in such a manner that the hydrocarbon contained in the small vessel spreads over its surface, and presents a large surface to the oxygen. When the exposure is deemed sufficient, the flask is straightened again, frozen under the same conditions as before, and the capillary tip of the tube sealed on at the side of the neck is broken off inside a thick-walled rubber tube. This tube connects the capillary to a manometer without adding appreciably to the total volume.

After 138 days of exposure on the roof of the University (from May 12, 1927 to September 27, 1927), we found a diminution of pressure of 61 mm. for the sample prepared from nickel, and 83 mm. for the other. These values correspond, respectively, to the absorption of 160 and 220 cc. of oxygen at 20° and 760 mm. These are, for the reasons indicated above, minimum values. The autoxidation is much more rapid here than it was in the experiments made in diffused light. The oxidized liquids give tests for peroxides, but do not contain hydrogen peroxide, for Crismer's reagent (citric acid–ammonium molybdate) gives negative results.

The peroxide is destroyed when the excess of hydrocarbon is distilled under atmospheric pressure, but if we carry out the distillation at 20-mm. pressure, warming the system to 40° and condensing the vapor at −78°, we obtain a residue which gives exclusively the reactions of a peroxide, to a high degree. This residue also contains other oxidized compounds. In fact, the titration of peroxides in a known weight of residue, employing an iodide solution acidified by acetic acid, leads to values of oxygen combined as peroxide which are much smaller than the amount of oxygen which disappeared, assuming that the peroxide acts on an acceptor by only one atom of active oxygen. In the case of the nickel sample about one-fifth of the oxygen that disappeared was found combined as peroxide.

Influence of Temperature on the Oxidation. Experiments in Diffused Light at 100°.—These experiments were carried out with considerably greater hydrocarbon masses, which required large volumes of oxygen. The apparatus consists of flasks of 2 or 3 liters' capacity, connected by their narrow necks to a vertical glass cylinder, 40 cm. long and 5 cm. in diameter, which acts as an air condenser. Its upper part, drawn out, carries a side tube which is closed by a stopcock near its free end, the stopcock being first tested for leaks. From this side tube a manometer tube leads to the mercury reservoir. After introduction of the hydrocarbon, the apparatus is sealed, evacuated after chilling and filled with oxygen in such a manner that the pressure inside will not exceed that of the atmosphere when the required temperature is reached. The volume of oxygen introduced is read on the gasometer. Measured quantities are later led in from time to time, depending on the pressure given by the manometer. On certain occasions, particularly when the speed of absorption has slackened sufficiently, the residual gases may be evacuated by a mercury pump, in order to refill the system with fresh oxygen, and to carry out analyses. The lower part of the flask is placed in an air-bath which reaches to the level of the free hydrocarbon surface. This air-bath is kept at the required temperature by an electric hot-plate. The temperature is given by a thermometer whose bulb is placed in the air-bath, where it touches the wall of the flask. It is kept between 100 and 110°.

When the gas is pumped out, the hydrocarbon liquid is previously cooled in a freezing mixture of ice and salt, and the evacuated gas, before it can reach the pump, passes through a tube cooled to −78° by carbon dioxide snow and acetone, which traps the entrained hydrocarbon vapor.

We give as an example the following table, which shows the progress of the absorption of oxygen by a sample of 50 cc. of hydrocarbon (38.7 g.), prepared by hydrogenation over nickel.

Date of introduction of oxygen	Time	Liters of oxygen introduced, corrected to N. T. P.
19-12-1927	1st day	1.465
30-12-1927	12th	0.590
6-1-1928	19th	.895
12-1-1928	25th	1.220
14-1-1928	27th	1.280
16-1-1928	29th	1.190
19-1-1928	32nd	1.090
27-1-1928	40th	0.790
10-2-1928	54th	.500
		Total, 9.020

With a freshly distilled hydrocarbon, the absorption of oxygen accelerates after a slow start, then it becomes slower and slower, and finally reaches a state where the manometer shows—not diminution—but an increase in pressure. There are gaseous products formed by the oxidation, and the volume of these produced in unit time may possibly exceed the volume of oxygen absorbed.

Analysis of the Gas Phase.—The analysis of gas (1345 cc.) collected at the end of the experiment cited above showed that it contained much carbon dioxide (840 cc.) but very little oxygen (35 cc.—about 0.5% of the oxygen introduced into the apparatus). *Saturated cyclic hydrocarbons act as an excellent absorbent for oxygen at 100°.*

In the gas residue left after treatment with alkaline pyrogallol ammoniacal cuprous chloride indicated the presence of a little carbon monoxide. Agitation with fuming sulfuric acid gave no further diminution of volume, but the gas still contained combustible components. Rough eudiometric analysis showed that the ratio of volume diminution by explosion to the subsequent diminution of potash corresponded to a mixture intermediate to methane and ethane. The gaseous residue is nitrogen which accompanied the oxygen used.

Carbon monoxide, present in gas mixtures at low concentrations, is probably incompletely removed by cuprous salts. Furthermore, the eudiometric analysis of the combustible gases remaining after such absorption was incapable of furnishing an accurate indication of their nature. To identify and analyze them really requires fractional combustion by copper oxide.

We obtained the necessary gas mixture by treating 30 g. of hydrocarbon, kept for many months in a partly filled flask with oxygen at 100° in an apparatus with a total capacity of 2700 cc. We show below the progress of oxygen absorption compared with that observed in the previous experiment. It shows the favorable influence on the speed of oxidation at 100° of the slight previous alteration of the hydrocarbon employed.

	Volumes of oxygen introduced corrected to N. T. P., cc.
1st day	1870
5th day	1370
7th day	1350
10th day	1140
13th day	1365
	Total, 7095

On the seventeenth day 480 of the 1200 cc. of gas present was pumped through a tube at −78° and extracted for gas analysis. This showed 37.8% of carbon dioxide and 19.2% of oxygen. After absorption of these two, the residual gas formed 43% of the initial amount.

Two hundred cc. of this residue was separated into two fractions by passing the sample slowly through a Moissan tube cooled to −183° in order to condense the homologs of methane; 90 cc. remained in the vapor phase.[5] The part remaining in the tube is recovered separately by warming and pumping. This second fraction had a volume of 110 cc. Each of these fractions was submitted to fractional combustion over copper oxide in a nitrogen atmosphere. It is known that hydrogen and carbon monoxide burn alone and completely at 275° under these conditions, and that it is necessary to work at 800° to obtain a complete and rapid combustion of methane and its gaseous homologs.

In this way we found for the uncondensed fraction: H_2, 18.4%; CO, 8.2% and CH_4, 2.85% (no volume variation by oxidation at 800°). For the second fraction the combustion at 275° showed H_2, 15.7%, and CO. 7.8%. The subsequent combustion at 800° gives an increase of 5.94% of the initial volume submitted to analysis and the

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[5] Analysis carried out by Mr. O. Miller. The results obtained in analyzing gases resulting from the oxidation of various cyclic hydrocarbons in this manner will soon be collected in a paper.

contraction produced by the potassium hydroxide is 14.6%. So there must be at least one saturated gaseous homolog of methane present.

This may be ethane, but is not pure propane. The second hypothesis would lead to the following percentages in the second fraction: CH_4, 5.7, and C_3H_8, 2.97. It would follow that methane is liquefied in the cooled tube until its partial pressure, corresponding to 2.85%, is 22 mm. According to the measurements of Karwat[6] on the vapor pressure of methane, this would indicate that the temperature of the tube was $-191.5°$. This is the boiling point of an equimolecular mixture of oxygen and nitrogen. But our liquid refrigerant was liquid industrial oxygen, with a very low nitrogen content. (It yields a gas containing 4.5% of nitrogen.) We are able to conclude, on the other hand, that ethane is present. The respective percentages would be: CH_4, 2.72, and C_2H_6, 5.94. Comparison of this value for methane with that observed in the uncondensed fraction indicates, then, that there was no liquefaction of this gas, and the results of analysis of the condensed fraction, recalculated on the assumption that the gas is freed of ethane by liquefaction, are in fairly good agreement with the results found for the gaseous fraction. Calcd.: H_2, 16.7; CO, 8.3; CH_4, 2.90. Found: H_2, 18.4; CO, 8.2; CH_4, 2.85. All these calculations give the gas obtained after oxidation the following percentage composition: CO_2, 37.8; N_2, 29.7 (by difference); O_2, 19.2; H_2, 7.3; CO, 3.4; C_2H_6, 1.4; CH_4, 1.2.

Its volume at the time oxidation was stopped, computed by calibration of the apparatus and changed to standard conditions of pressure and temperature, was 1200 cc.

From this we deduce that, of the 7095 cc. of "oxygen" introduced, 355 cc. was nitrogen, leaving 6740 cc. of pure oxygen: 230 cc. was recovered, so 6510 must have been used up. About 455 cc. of carbon dioxide and 40 cc. of monoxide were formed at the expense of 475 cc. of oxygen. This means that about 6 liters took part in the formation of solid and liquid oxidation products. Simultaneously, about 90 cc. of hydrogen, 15 cc. of methane and 17 cc. of ethane were formed.

This experiment also enabled us to establish the formation of water during oxidation of the hydrocarbon. The liquid oxidation products were gently distilled under atmospheric pressure, and first began to pass over at 85°. At first a heterogeneous mixture was collected, but the distillate soon became homogeneous. We collected everything which distilled up to 102–103° and separated the two layers which had formed. The lower layer is composed mainly of water, freezing slightly below 0°; the upper layer consists wholly of hydrocarbons which have escaped oxidation and have been carried over by the water. We found about 1.10 g. of water.

Study of the Solid and Liquid Phases of the Oxidized System.—For this work we used the product obtained from 100 cc. or 77.5 g. of hydrocarbon prepared from nickel which, after absorption of 14.680 liters of pure oxygen, weighed 92.2 g., and the product obtained from 50 cc. or 39 g. of hydrocarbon prepared from platinum which, after absorption of 6.870 liters of oxygen, weighed 46.5 g. We thus had a total of 138.7 g. of oxidation product with which to work. It was a clear yellow liquid, more viscous than the hydrocarbon, and contained white crystals. Preliminary observations having revealed that these crystals are only slightly soluble in cold ether, while the liquid is completely miscible with this solvent, we rinsed out the flasks with ether, separated the crystals by filtration, and washed them with a little cold ether. They weighed 3.2 g. The ethereal solution is acid. It is agitated with a slight excess of potassium carbonate solution to dissolve the acid products. This solution is decanted, the alkaline liquid L_A is agitated with fresh ether to dissolve as much of the neutral products which it contains as possible, and this ether is added to the preceding ethereal solution, L_N.

Alkaline Solution—L_A.—It is gradually acidified with normal sulfuric acid in the

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[6] Karwat, *Z. physik. Chem.*, 112, 488 (1924).

presence of methyl orange. During the addition of the acid it becomes turbid and gives off the odor of fatty acids. It is extracted several times with ether, and the resulting ethereal solution L_A^2 is rapidly dried by agitation with calcium chloride. The aqueous solution L_A^1 is distilled.

Solution L_A^1.—The water which distils over contains *acetic acid* (0.062 g. mole). It is distinguished after neutralization by precipitation and analysis of the silver salt. Calcd.: Ag, 64.7. Found: Ag, 64.4, 64.6.

The precipitation of silver salts is accompanied by reduction and the precipitate must be recrystallized twice in succession by cooling the boiling filtered solution. This reduction must be attributed to substances other than formic acid, in large part at any rate. The action of mercurous chloride on a neutralized sample of the liquid, taken before precipitation, gives doubtful results.

The residue from distillation is composed of crystals of potassium sulfate impregnated with an odorous oil, which was extracted with ether. After getting rid of the ether, we are left with about 2.5 g. of a slightly volatile product which distils under a pressure of 3 mm.

Between 130 and 150° we obtain a viscous acidic liquid (H_1) (see below, ketonic acids), accompanied by neutral crystals melting between 145 and 155° (H_2). These products will be met again and will be studied later.

L_A^2 Ethereal Solutions of Easily Extractible Acids.—The ether is separated by means of a fractional distillation column, and the residue is first distilled under atmospheric pressure up to 153°. Between 70 and 120° there distil a few drops of a liquid with a sharp odor, which reacts as an aldehyde in the presence of decolorized fuchsine, but contains no formic acid. Between 120 and 153° a liquid distils (1.25 g.), which requires 0.011 g. mole of sodium hydroxide for neutralization.

After neutralization, ether extraction leaves some insoluble droplets of an odorous neutral liquid, while the alkaline salt remaining in solution is changed to the silver compound. There is no reduction. Analysis gives Ag, 63.2, 63.5%.

During the calcination we noticed a fatty acid odor. It is due to silver acetate (Ag, 64.7), containing, no doubt, a small amount of the silver salt of a higher acid.

We continued the distillation under reduced pressure with these results:

I.	From 52 to 105°, and mainly from 100 to 105°	23 mm.	1 g.
II.	From 100 to 142°, and mainly from 109 to 120°	18 mm.	1 g.
III.	From 126 to 149°, and mainly from 140 to 149°	5 mm.	3.6 g.
IV.	From 146 to 165°	5 mm.	3.25 g.

The residue weighed about 1 g.

By employing the formation of the silver salts of I and II, we have detected the presence of a hexanoic acid. Calcd. for $C_6H_{12}O_2Ag$: Ag, 48.4. Found: 48.2, 48.3, 48.5.

The remainder of each of these fractions was treated with thionyl chloride and the reaction product mixed with aniline to form the anilide of the acid. This anilide was purified by crystallization in light petroleum ether; the crystals obtained from I melted at 84.5°, those from II at 82.0°. The quantity at our disposal did not permit recrystallization to the point where constant values would be obtained, but by testing a mixture consisting of the crystals melting at 84.5°, and those of the anilide of synthetic β-methylvaleric acid (m. p. 86.6°), their identity was revealed, for the mixture melted at almost exactly 86°, when the two components were present in equal amounts.

This shows that one of the products of the oxidation of the hydrocarbon is

$$CH_3CH_2CH(CH_3)CH_2COOH$$

The greater part of Fraction III (3.1 g.), was neutralized by a 1 *N* solution of potassium hydroxide, 19.35 cc. of the latter was required, which gives a molecular weight of

160. It is a maximum value of the equivalent weight of an acid contained in this fraction. The neutralized solution is extracted with ether to eliminate as much of the neutral impurities as possible, then reacidified with sulfuric acid, and again extracted many times with ether. After drying the ethereal solution over calcium chloride, the ether is expelled and the residue distilled under reduced pressure. At a temperature of 167–170° and under a pressure of 13.5 mm., 2.3 g. was collected. The molecular weight determined by titrating 0.4435 g. with 0.1 *N* potassium hydroxide (27.9 cc.) was 159. This acid is water soluble.

It is a ketonic acid. It gives a semicarbazone which shows an instantaneous (30 sec.) melting point of 153°, when purified by crystallization in methyl alcohol. This semicarbazone has acid properties. Its molecular weight, found by the neutralization of 0.3054 g. with 14.25 cc. of 0.1 *N* potassium hydroxide, is 214.

This ketonic acid contains the acetyl group. Iodine in alkaline solution gives the iodoform test. Therefore it may be represented by $CH_3COC_6H_{10}COOH$ (mol. wt., 158). We have established the constitution of this acid by synthesizing it from 1,4-dimethylcyclohexene-1. This unsaturated hydrocarbon, which is prepared by making use of the catalytic dehydrating action of *p*-toluenesulfonic acid on 1,4-dimethylcyclohexanol-1, boils at 127.6–128.1° under 753.4-mm. pressure. Its density is d_4^{15} 0.8051.[7]

Twenty-two grams of this hydrocarbon was oxidized by the theoretical amount of a 2% solution of potassium permanganate, the first part of the latter being added during one day at a temperature near 0°. The rest was mixed in at room temperature. The colorless liquid obtained was siphoned from the dioxide sediment, the latter washed by decantation and finally separated by filtration.

The mixture of alkaline liquids was concentrated to a volume of 400 cc. on a water-bath in a current of carbon dioxide; after extraction with ether to remove as much of the neutral products as possible, the liquid was freely acidulated with sulfuric acid, saturated with ammonium sulfate and finally was extracted with ether several times. After drying the ethereal solution over calcium chloride, the ether was evaporated and the residue distilled under reduced pressure. Under 12-mm. pressure, 0.7 g. was collected up to 85°, and under 5 mm., 5.75 g. up to 175°.

This last fraction is formed of a mixture of liquid and crystals, petroleum ether dissolving the latter without mixing with the liquid. The crystals can therefore be extracted with petroleum ether; the dense layer of the initial liquid, separated by decantation, is warmed to rid it of dissolved petroleum ether, placed in a water–alcohol solution, and treated with semicarbazide hydrochloride and sodium acetate. The precipitate of semicarbazone is separated, washed with ice water, and purified by crystallization in methyl alcohol.

The point of instantaneous fusion (30 sec.) of the crystals is 152.5°. The mixture of these crystals with those of the semicarbazone of the ketonic acid obtained by oxidation, melt at the same point. The two ketonic acids are identical. Thus the oxidation of 1,4-dimethylcyclohexane by oxygen gives the β-methyl-δ-acetylvaleric acid

$$CH_3COCH_2CH_2CH(CH_3)CH_2COOH$$

This ketonic acid, which is not described in the literature so far as we know, was prepared in the pure form by the hydrolysis of the semicarbazone by hydrochloric acid. It boils at 141.2° under 2.5-mm. pressure.

From Fraction IV of the distillate of acids obtained under reduced pressure, we isolated 2.5 g. of the same acid ketone; b. p. 137.8–141.2° under 2-mm. pressure; mol.

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[7] Sabatier gives b. p. 125° under 760 mm., d_4^0 0.8207, d_4^{14} 0.8111; *Compt. rend.*, **141,** 21 (1905); **142,** 438 (1906); *Ann.*, [8] 10, 558 (1907). Zelinsky gives b. p. 128.5°; d_4^{20} 0.8005; *Ber.*, **41,** 2632 (1908).

wt., 156; semicarbazone, m. p. 152.5°. Neither in this fraction nor in the residue has any other acid been identified.

The viscous acid liquid H, obtained above in the distillation residues of the aqueous acid solution L_A^1, a liquid which distils between 130 and 150° (3 mm.), is formed largely of β-methyl-δ-acetylvaleric acid.

L_N Ethereal Solution of Neutral Products.—This solution is dried over sodium sulfate, and the ether is expelled on the water-bath. The distilled ether is then gently rectified with a large Crismer column. This leaves a residue which is then fractionated. Under normal pressure, we obtain 8 g. of a water-insoluble liquid between 120 and 123°, its density being d_4^{15} 0.7734. This is the non-oxidized hydrocarbon. There remains a slight residue of long needle-like crystals, melting near 50° (see below, 1,4-dimethylcyclohexanol-1).

After evaporating the greater part of the ether from L_N on the water-bath, the distillation is continued with a paraffin-bath at atmospheric pressure, the temperature being gradually raised to 165–170°. Up to 94° we obtained 7.5 g. of a liquid composed almost entirely of ether. From 94 to 123°, 9.5 g. of a heterogeneous liquid came over. It contained an aqueous layer weighing 1 g., and a layer of lower density.

The aqueous layer contained formic acid, as was clearly shown by the reduction of mercuric chloride in the presence of formate-free sodium acetate. The upper layer (8.5 g.) consists principally of regenerated hydrocarbons, but it contains—like the aqueous layer—an aldehyde, which is shown by its action on Schiff's reagent. It was not possible for us to determine the nature of this aldehyde, due to its low concentration.

The distillation is then carried further under reduced pressure, the flask acting as receiver, being followed by a Moissan tube immersed in a freezing mixture. Commencing at 40 mm., the pressure was gradually reduced as the boiling point rose. The results were: I, in the Moissan tube, we obtained 3.4 g. of a heterogeneous liquid mixture; II, from 70° and 40 mm., to 85.5° and 31 mm., 22.7 g. of a substance which was solid at room temperature; III, from 85.5° and 31 mm. to 92° and 18 mm., 20.1 g. of a solid (at room temperature); IV, from 92 to 98° and 18 mm., 3.6 g. of a liquid containing some suspended crystals. The distillation stopped here sharply, and did not resume until the temperature had reached 120°, under 2-mm. pressure. Let us first consider the neutral volatile products distilling below 98° (18 mm.).

In the heterogeneous fraction, I, we found about 2 g. of the original hydrocarbon forming the greater part of the upper layer. The lower layer is an aqueous solution. Each contains a ketone which gives an instantaneous precipitate of a very insoluble semicarbazone when treated with semicarbazide hydrochloride and sodium acetate. This same ketone was found in the other three fractions.

Fractions II and III are dissolved in ether, and the solution is shaken with a concentrated solution of sodium bisulfite. A crystalline precipitate is formed and is collected and washed with ether. With this solvent (ether), the aqueous bisulfite layer is extracted, and these ether washings are added to the main ethereal solution. The precipitate and the bisulfite waters are separately distilled with a 2 *N* solution of potassium carbonate.

In both cases the first runnings give a heterogeneous mixture of water and ketone; later we get nothing but an aqueous solution. The successive fractions give immediate precipitates with semicarbazide. The distillation is continued as long as an appreciable precipitate is formed. The semicarbazone is separated, dried, washed in cold water and then recrystallized in a large excess of boiling water. After being desiccated, it shows a constant decomposition point of 243° (twenty sec.). The rapidity of precipitation of this semicarbazone, its insolubility in cold water, and its very slight solubility in boiling water, the ease of distillation with steam exhibited by the corresponding ketone, its distinctive solubility in water—all these properties are characteristic of acetonylacetone. But the decomposition point of the semicarbazone of the latter, according to the literature, is 223°. In order to check this value, the substance was prepared synthetically, beginning with ethyl acetoacetate and following the procedure of Knorr. Its semicarbazone has a decomposition point of 242°. The value given in the literature should be corrected. The mixture test indicated the identity of the two products. The oxidation of 1,4-dimethylcyclohexane at 100° yields acetonylacetone, $CH_3COCH_2CH_2COCH_3$. The quantity obtained, estimated by the weight of the semicarbazone, is of the order of half a gram.

The non-ketonic part of fractions II and III is in solution in ether. After drying this solution over potassium carbonate, it is distilled under atmospheric pressure until the ether has gone, and then low pressures are used. In this way the small interval between 83.4° under 45.5 mm. and 79.2° under 43.5 mm. yields an important fraction weighing 25 g. It solidifies completely in the receiver. In a Moissan tube, immersed in a freezing mixture and connected to the receiver, 3 g. of a liquid is collected simultaneously. A distillation residue of 4 g. remains. The rectification of the first fraction collected in the freezing mixture and the tailings under atmospheric pressure gives on the one hand 2.5 g. of the original hydrocarbon and, on the other, 2.6 g. of the preceding solid. We thus obtain a total of 21 g. of the hydrocarbon submitted to oxidation, out of 116 g. put into the experiment.

The solid collected is distilled under atmospheric pressure. It distils from 170 to 172° under 760 mm. (corrected), and melts between 51.7 and 53°. It has an appreciable vapor pressure at ordinary temperatures and evaporates readily in the air. It is easily carried over by ether vapor. When sublimed it forms needles several centimeters long. It has a camphor-like odor.

Anal. Subs., 0.1301: H_2O, 0.1473; CO_2, 0.3571. Calcd. for $C_8H_{16}O$: C, 75.00; H, 12.5. Found: C, 74.92; H, 12.58.

It reacts as an alcohol. Its allophanate, when recrystallized from methyl alcohol, melts at 163° (in twenty seconds). This carbinol has been identified with 1,4-dimethylcyclohexanol-1.

Sabatier and Mailhe,[8] who prepared this compound, give its melting point as 50°, and its boiling point under 760 mm. as 170°. We have prepared it by synthesis from methylmagnesium iodide and *p*-methylcyclohexanone. The product melts at 52.8° and boils at 168.2–168.8° under 730-mm. pressure. The mixture of this synthetic compound and the carbinol obtained by oxidation melts between 51.7 and 53°. These two substances are easily dehydrated by warming with a trace of *p*-toluenesulfonic acid, each giving the same olefin with a boiling point between 127.6 and 128.1° under 753.4-mm. pressure.

The action of oxygen at 100° on 1,4-dimethylcyclohexane yields, therefore, an important quantity of 1,4-dimethylcyclohexanol-1. The latter is by far the preponderating oxidation product. Furthermore, it has been detected in the hydrocarbon oxidized at ordinary temperatures. The part of the hydrocarbon molecule sensitive to oxidation is thus the tertiary group, $—CH<$.

Fraction IV from the distillation of the neutral volatile products contains a little β-methylvaleric acid which has escaped from the carbonate extraction, a little acetylacetone, some crystals with a melting point of 193° identical with those separated by filtration of the crude product of oxidation, and 0.3 g. of a neutral non-carbonyl liquid with a camphor-like odor, which passed over at 180–187° under normal pressure. It has not been identified.

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[8] Sabatier and Mailhe, *Compt. rend.*, 141, 21 (1905); *Ann. chim. phys.*, [8] 10, 558 (1907).

Neutral Products of Low Volatility.—After distilling Fraction IV, a yellowish-brown sirup is left behind. It forms a homogeneous solution when treated with a mixture of ether and petroleum ether. Crystals soon begin to deposit from it. The crystallization is continued at 0° with frequent shaking and the crystals are separated by filtration and washed with a little cold ether. Two g. was collected in this way. These crystals are not pure—as their melting point ranges from 143 to 156°. It is the same crystalline mixture which we found above in the residue left by the distillation of the volatile acids. These solid substances were dissolved by the potassium carbonate solution during the extraction of the acids. They are neutral, but soluble in water.

After driving off the solvents, ether and petroleum ether, by distillation, the residue is extracted with hot water. The aqueous solution is separated and evaporated on the water-bath. A residue is left which crystallizes in the desiccator (about 0.5 g.). After drying on a porous plate and washing with a little cold ether (about 0.5 g.), it still melts over the interval 143–155°. They are united with the preceding ones. Fractionation of the neutral liquid is then carried out by successive extraction with a 2 *N* potassium carbonate solution, then by entrainment in steam, and finally by distillation under 4-mm. pressure until the temperature has reached 200°. A very viscous deep brown residue remains.

The fraction extracted by the carbonate (3 g.) distils between 107.5° under 11 mm. and 150° under 2 mm. The fraction carried over by steam (2.3 g.) distils between 120 and 150° under 15-mm. pressure. The fraction distilling under 4 mm. (5.5 g.) is rectified. It distils regularly between 135° (12.5 mm.) and 196° (2 mm.).

No definite product could be isolated and identified in these fractions. Substances with the properties of esters occur in the last two. The product of the saponification of the fraction carried over by steam contains a fatty acid salt with a caproic odor, and a neutral alcoholic product distilling between 130 and 133° (17–18 mm.) which crystallizes partially at room temperature. Two analyses of this neutral product gave H, 11.24, 11.21; C, 69.17, 69.43, without throwing any light on its constitution.

The saponification products of the rectified fractions of the liquid distilling under 4 mm. up to 200° contain salts of ketonic acids, and the neutral alcoholic part also crystallizes partially at ordinary temperatures.

Neutral Crystalline Products.—We have on the one hand the crystalline component separated from the ether-treated oxidation product by filtration (3.2 g.). This component, which is slightly soluble in ether, melts at 193 ± 1°. We have, on the other hand, crystals which can be extracted by water, and which are precipitated from the neutral, slightly volatile products by treatment with ether and petroleum ether at 0° (2.5 g.). They melt at 143–156°.

The first were purified by solution in pure, dry, boiling acetone, and subsequent crystallization from the cooled, agitated solution.

The others are equally soluble in cold acetone, and crystallize incompletely on cooling, or by evaporation only, if the solution is dilute. Crystallization by cooling the concentrated solution gives pure crystals on rare occasions, and it is only by slow, patient evaporation of a dilute solution that separation of the original substance into two pure constituents can be completely effected. Since crystals formed in this manner are relatively large, they may be easily recognized as being of two types, which can be separated by hand picking. The monoclinic form melts at 193° ± 1. They are identical with those obtained by filtration of the crude oxidation product, and are the less soluble. The others form tetragonal groups of four orthorhombic units, and melt at 165.5–166°.[9] These two pure substances act in an analogous manner in the presence of

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[9] We are indebted to Mr. Gilta, Assistant Professor at the University of Brussels, for these crystallographic data.

solvents. Only slightly soluble in ether, they are more so in acetone and quite soluble in hot water; 100 g. of boiling water dissolves approximately 3.5 g. of the crystals which melt at 193°, and more than three times as much of the other variety. They sublime simultaneously under reduced pressure with a speed which is already appreciable at 100°.

The crystals melting at 193°, obtained by slow evaporation of the acetone solution, rapidly become opaque near 95°. It is a polymorphic transformation, and is not accompanied by any elimination of water or acetone of crystallization; then, as the temperature is increased, the crystals sublime, giving needles which radiate from a central point. The fusion point, which must be determined by heating rapidly enough to avoid complete vaporization, evidently depends on the amount of the latter form present.

The two substances are isomers with the molecular formula $C_8H_{16}O_2$. Their percentage composition has been determined by the method of Ter Meulen and Heslinga.[10]

Anal. of the 193° variety. Subs. I (large crystals obtained by slow crystallization from acetone), 0.0594: H_2O, 0.5094; CO_2, 0.1448. Found: H, 11.18: C, 66.48. Subs. II (needles obtained by sublimation in a stream of nitrogen), 0.0525: H_2O, 0.0524; CO_2, 0.1288. Found: H, 11.09; C, 66.91.

Anal. of the 165.5–166° fraction. Subs. I, 0.0554: H_2O, 0.0547; CO_2, 0.1354. Found: H, 10.97; C, 66.65. Subs. II, 0.0628: H_2O, 0.0625; CO_2, 0.1533. Found: H, 11.13; C, 66.52. Calcd. for $C_8H_{16}O_2$: H, 11.18; C, 66.61.

The approximate molecular weight was determined by microebullioscopic methods in aqueous solution in a modified Cottrell apparatus which contained a micro Beckmann thermometer. The values obtained are not very precise, due to the slight solubility of the 193° compound, the smallness of the ebullioscopic constant of water, and the small amount of the substance at our disposal. However, these values seemed to us to be sufficient to establish the molecular formula of the two compounds as $C_8H_{16}O_2$.

193° Compound—0.1529 g. dissolved in 5.090 g. of water raised the boiling point 0.105°. Therefore, mol. wt. = 149.

165.5–166° Compound: I—0.251 g. dissolved in 5.040 g. of water raised the boiling point 0.19°. II—0.443 g. dissolved in 5.04 g. of water raised the boiling point 0.275°. Therefore, from I: mol. wt. = 136 and from II—mol. wt. = 166. Calculated for $C_8H_{16}O_2$ = 144.

These two isomers are two glycols, $C_8H_{14}(OH)_2$. The solubility characteristics of these two compounds led to this conclusion. We first tried to verify it by employing Zerewitinoff's hydroxyl determination method, using iso-amyl ether as the solvent for methylmagnesium iodide, and working in an atmosphere of pure nitrogen. The more soluble compound (165.5–166°) reacts fairly rapidly on the Grignard reagent at ordinary temperatures, 0.0918 g. giving 28.3 cc. of methane (N. T. P.). The calculated value for $C_8H_{14}(OH)_2$ is 28.6 cc. This compound is thus a 1,4-dimethylcyclohexanediol. The less soluble compound (193°), reacts only to a negligible extent under similar conditions. Even on warming the system, only a small fraction of the required volume of methane is liberated in a day. This has not seemed to us sufficient to conclude that we were not dealing with a di-alcohol, for its insolubility in the iso-amyl ether will furnish an explanation, since finely powdered saccharose acts in the same way.

When the 193° compound is powdered and added to a concentrated solution of hydrochloric acid, it dissolves very rapidly at room temperature, although it does not dissolve at all in water under the same conditions. Then the solution becomes cloudy, and finally begins to deposit minute crystals which are only very slightly soluble in the excess of hydrochloric acid. They are easily separated by filtration and drying on a

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[10] "Nouvelles methodes d'analyse chimique organique," by H. Ter Meulen and J. Heslinga, translated from the Dutch by T. Kahan, Dunod. Paris, 1927.

porous plate. They are finally placed in a desiccator containing fused potash. These crystals, which have a camphor-like odor, are insoluble in water, but soluble in alcohol and ether. They melt between 46 and 49°, and have an appreciable vapor pressure at ordinary temperatures. They contain some chlorine, but the latter is not easily detectable in a dilute alkaline solution at room temperature; this crystalline compound, whose formation is so easy, is not an oxonium salt. On the contrary, it may be saponified by an alcoholic solution of potassium hydroxide or sodium methoxide; this reaction takes place little by little at room temperature, is fairly rapid at water-bath heat, and was employed by us for chlorine determination by weighing the silver chloride formed from the chlorides. Subs., 0.1151: AgCl, 0.1808. Calcd. for $C_8H_{14}Cl_2$: Cl, 39.18; for $C_8H_{14}ClOH$: Cl, 21.8. Found: Cl, 38.85. So we are dealing with a dichloro ester, and the compound $C_8H_{16}O_2$ which melts at 193° is thus a 1,4-dimethylchlohexanediol.

Concentrated hydrochloric acid affects the more fusible isomer, $C_8H_{16}O_2$, just as it does the one above. We prepared a small quantity of its dichloro ester by the action of 1 g. of concentrated hydrochloric acid on 0.118 g. of this glycol. The crystals so obtained melted at 38.6–39.3°. They are saponified by sodium hydroxide in alcoholic solution. A determination of chlorine in these crystals has been made by using this saponification and precipitating the chloride ions as silver chloride. Subs., 0.0579: AgCl, 0.0901. Found: Cl, 38.5.

What might the constitution of these two isomers be? A group of facts has led us to consider them as bitertiary glycols. These facts are: (1) the preponderating formation of tertiary alcohol in the oxidation of the hydrocarbon. This indicates that the group —CH< is the particular center of attack on the molecule. All experiments which we have made on the oxidation of cyclopentane and side-branch cyclohexane hydrocarbons confirm this. (2) The formation of acetonylacetone during oxidation: this indicates attack of the oxygen on two —CH< groups para to each other. (3) The almost instantaneous transformation of the two isomeric diols into their chlorine derivatives by the action of concentrated hydrochloric acid, is not compatible with the properties of primary or secondary alcohols, according to classical observations. (4) In the products obtained by applying Wagner's reaction to 1,4-dimethylcyclohexene-1, we have not found any trace of these two diols. They are not the 1,2-diols. This reaction of Wagner tells us at the same time that if the 1,2-glycols are formed during the oxidation of the hydrocarbon by oxygen, they have only a transitory existence.

General Conclusions.—We may finally sum up in general fashion the oxidation of 1,4-dimethylcyclohexane by oxygen at 100°.

Of 116 g. of hydrocarbon at the beginning, 21 g. was recovered unchanged, which means that 95 g. was oxidized by 21.5 liters of oxygen, or about 25 liters of oxygen per molecular weight. The sum of the weights of the hydrocarbon which was affected and the oxygen used up is $95 + 30.7 = 125.7$ g. Oxidized liquid and solid products made up $138.7 - 21 = 117.7$ g., while the weight of the carbon dioxide formed is 5.2 g. Since the weight of the other gases is negligible, the total is 123 g.

The oxidation product which is present in the greatest proportion has been identified as 1,4-dimethylcyclohexanol, which gave about 30 g. of the pure product. The quantity formed, however, is doubtless much larger.

In order of decreasing weight, neglecting the water, the products are: as acids—β-methyl-δ-acetylvaleric 8 to 9 g., acetic 4–5 g., methyl-2-valeric about 2–3 g.; as neutral products—the 1,4-diol (m. p. 193°) 3.5 g., a second 1,4-diol (m. p. 165.5°) 2.0 g., acetonylacetone about 0.5 g.

Consideration of the oxidation products which we have succeeded in identifying shows that we may represent the reaction as a progressive splitting up of the hydrocarbon molecule. In the first phase, a peroxide results from the addition of an oxygen molecule to one tertiary —CH< group of the hydrocarbon. Then the peroxide decomposes according to one of the following processes. (1) It acts as an oxidizing agent in losing an atom of oxygen, and changes to a tertiary alcohol. The acceptor may be either another hydrocarbon molecule or an oxidation product already formed. The latter is in particular the carbinol, acting through its free tertiary group to give a 1,4-diol. (2) It may join the second oxygen atom to a neighboring carbon atom, the splitting of the ring between the two oxygen-bearing carbons being the first step in the formation of the ketonic acid we have found. (3) To account for the formation of β-methylvaleric acid, we must also assume a possible opening of the ring by the ketonic split of the tertiary carbinol (or of a 1,2-diol, resulting from the preceding method of evolution between the carbon atoms 1 and 6).

Admitting the same sensitivity of the tertiary group to oxygen when it is in the products of ring-splitting, and a repetition of the aforementioned reactions, we may account for the formation of acetonyl acetone, ethane, methane and acetic acid.

The appearance of hydrogen during oxidation is more mysterious. The phenomena of photolysis and autoxidation have been thoroughly investigated for alcohols at ordinary temperatures, but they seem to produce hydrogen only in the presence of acceptors, such as ketones which are transformed into pinacones.[11] The existence of free hydrogen in these systems has not been observed, as far as we know. Alcohols are dehydrogenated by copper heated to a point below 200°. Can this phenomenon take place, with a very feeble velocity, below 100° and in the absence of catalysts?

A very recent note by Briner and Schnorf,[12] which we have seen during the writing of this paper, contains a result equally unexpected, a result which should be compared with ours. These authors have observed that the ozonization of ethylene in the presence of a trace of water

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[11] Ciamician and Silber, *Ber.*, **34**, 1530 (1901); **36**, 1575 (1903); W. D. Cohen, *Rec. trav. chim.*, **38**, 27, 113 (1919); Böeseken, Cohen and Langedijk, *ibid.*, **44**, 173 (1925).

[12] Briner and Schnorf, *Helv. Chim. Acta.*, **12**, 154 (1929).

gives the dioxymethyl peroxide of Wieland and Wingler,[13] and that the liberation of hydrogen by the ozonide, a reaction which they established in a manner to dispel any doubt, is related to the decomposition of this product. This suggests that the formation of hydrogen may well be connected with a rearrangement of the primary peroxide in our case. Experimental work in progress can at least limit the field of hypothesis in this connection.

Summary

The experiments reported in this paper have shown that 1,4-dimethylcyclohexane absorbs oxygen at room temperature in diffused light. This absorption is slower than that previously determined under the same conditions for 1,3-dimethylcyclopentane. It is accelerated by direct sunlight. At 100° it becomes rapid. If the hydrocarbon is very pure, there is an initial period during which the absorption is slow. This induction period is greatly shortened by the presence of hydrocarbon which has already been oxidized.

The saturated hydrocarbon acts as an excellent absorbent at 100° in weak light, being capable of extracting all but a few parts per thousand of any oxygen present. Among the oxidation products we have isolated the following gases: CO_2, CO, H_2, CH_4, C_2H_6. The liberation of hydrogen during the oxidation is particularly to be noticed.

In the liquid and solid phases we have identified, aside from water, (a) acid products—traces of formic acid, acetic acid, β-methylvaleric acid, and β-methyl-δ-acetylvaleric acid, $CH_3COCH_2CH_2CH(CH_3)CH_2COOH$, which is not described in the literature, and whose synthesis we have effected; (b) neutral products—1,4-dimethylcyclohexanol-1, the stereoisomeric 1,4-dimethylcyclohexandiols-1,4, which have not been described in the literature, and acetonylacetone (*sym.-diacetylethane*).

We have prepared and briefly described the stereoisomeric 1,4-dimethyl-dichloro-1,4-cyclohexanes, obtained from the corresponding diols. The preponderating oxidation product is 1,4-dimethylcyclohexanol-1.

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[13] Wieland and Wingler, *Ann.*, **431**, 301 (1923).