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Report

on

The Oxidation and Gumming Tendency of Certain Typical Component Hydrocarbons of Aviation Gasoline.

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ABSTRACT

A series of typical component hydrocarbons present in aviation gasoline has been synthesized and then subjected to accelerated oxidation at 100°C. for 24 hours. The oxygen pressure was 100 pounds guage at 25°C. at the beginning of the test. At the end of that time the treated materials were examined chemically and spectroscopically for evidences of instability and gum formation. A few hydrocarbons such as isooctane, benzene, cyclohexane, and cyclopentane were stable. But the majority of the benzenoid and cyclic saturated hydrocarbons absorbed oxygen to a greater or less degree. The amount of absorption appeared to increase as the complexity of the molecular structure of the materials examined increased. In spite of the reactivity with oxygen, negligible amounts of gum were formed. The olefinic hydrocarbons on the other hand, not only displayed high oxygen absorptions but also deposited considerable amounts of gum. The olefines of the cyclopentane series were the least stable, both in regard to oxygen absorption and gumming tendency followed by styrene, the cyclohexenes, and diisobutylene.

Certain interesting generalities and the relationship of molecular structure to the stability of hydrocarbons has been noted.

A discussion of the possible effects of certain of the hydrocarbons examined in relation to storage problems of aviation gasoline has been included.

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INTRODUCTION

(a) Authorization

1. The study covered by this report was authorized by Bureau of Aeronautics letter Aer-E-46MN JJ7G1 of 30 September 1936.

(b) Statement of Problem

2. This report concerns a study of the reactions of certain hydrocarbons toward oxygen at 100 pounds per inch pressure at a temperature of 100°C. The work was undertaken to determine the stability of typical hydrocarbons which are likely constituents of aviation base stocks and finished fuels, to extend certain similar studies which have been reported in the literature to include complex naphthenes and substituted aromatics which have been little investigated, and to correlate the structural characteristics of hydrocarbons with the degree of resistivity to attack by molecular oxygen under conditions more severe than are experienced by long standing in contact with air at ordinary temperatures. Ultimately it is hoped that some relationship may be deduced which will allow a correlation of the accelerated aging test in the oxygen bomb with the actual behavior on long-time storage.

(c) Known Facts Bearing on the Problem

3. A gasoline is considered stable on storage if, at the end of the storage period, the original characteristics of the fuel are unaltered; in other words, the distillation range shall be unchanged, the color stable, the octane rating unaffected, and the gum content shall not have risen above the specification limit. Alterations of these characteristics can be ascribed to (1) changes due to evaporation losses; (2) the reaction of certain of the component hydrocarbons of the gasoline with atmospheric oxygen; and (3) obscure polymerization reactions, involving the unsaturated and possibly the aromatic and naphthenic fractions, which usually proceed through the intervention of oxygen and are probably influenced by that already oxidized portion of the fuel. Changes due to evaporation losses are easily detected by inspection of the Engler distillation curve and are generally controllable by storage under proper conditions. Alterations of color, lead value, octane rating, gum and gumming tendency are ascertained by standard tests but the prevention of such changes is often difficult. Some degree of success has been obtained by the addition of minute amounts of anti-oxidants, negative catalysts or inhibitors to the unstable fuel. Such practice serves very well for gasolines designed for immediate commercial consumption; it is of doubtful value when long-time storage is contemplated. For, the protection afforded is by no means permanent and the inhibiting agents used

sometimes actually accelerate the rate of deterioration when once the process finally sets in. Furthermore, these inhibitors in aviation gasoline, being indifferently volatile solids or high boiling liquids at manifold temperatures, tend to deposit in the intake systems during motor operation. These deposits are of little moment in engines as rugged as the standard automobile types, but in a mechanism so comparatively delicate and sensitive to the changes in the nicety of its adjustments as an airplane motor, the accumulation of such deposits is not desirable. The problem appears, then, to resolve itself into (1) determining what particular types of gasoline hydrocarbons are unstable, and (2) formulating means for their detection in gasolines designed for military use or fighting grade stocks not intended for immediate consumption.

4. Considerable work has already been done in this Laboratory on detecting deleterious changes that occur in gasoline. These results have been presented in Naval Research Laboratory reports numbers P-1394, P-1499, and P-1500. The present report approaches the problem in a somewhat different manner, that is, the tantamount consideration is the type of hydrocarbons which may cause trouble rather than the degeneration products. Herein, are presented the preliminary phases of that work in which certain pure type hydrocarbons have been synthesized, their physical characteristics determined and compared with values occurring in the literature, and the stability of them towards oxygen at 100 pounds initial guage pressure at 100°C. for 24 hours investigated.

(d) Theoretical Considerations

5. It is commonly accepted that the underlying cause of gum formation and cognate alterations is generally due to the interaction of oxygen with certain hydrocarbons in the gasoline. That oxygen does have a prominent function in initiating gum formation is indicated in the work of Smith and Cook[1] who examined the stability of certain cracked gasolines when stored in the presence and absence of air. That this role of causative agent continues through the whole period when gum is being formed and deposited is shown in the fact that gums isolated from various gasolines contain amounts of oxygen varying from 15 to 30 per cent (Storey, Provine and Bennet)[2]. Only in instances of highly cracked stocks containing dienes, trienes, and more highly unsaturated substances, or where cyclic structures of the styrene or cyclopentadiene type occur, is the possibility of polymerization and gum formation in the absence of oxygen at all likely under usual conditions.

6. The mechanism of gum foration is still but vaguely understood. Very credible and intriguing theories explaining the oxidation of olefines have been advanced which postulate the initial formation of peroxide by the addition of oxygen to

the double bond. Some of these peroxides may polymerize to oxygenated bodies of high molecular weight; others are known to be unstable, breaking down into alcohols, ketones, aldehydes and acids, or capable of reacting with other olefine molecules, as has been demonstrated by Pirlescheav[3], to give aldehyde oxides which are in some cases so unstable as to decompose spontaneously to aldehydes of lower molecular weight. The initiation of such reactions requires the addition of a certain amount of energy which may be derived from actinic light, the thermal conditions of the place of storage, or, as in the case of this report, from the heat of the surrounding bath. Once started, the action is probably auto-catalytic and very likely proceeds through a chain mechanism.

7. The oxidation of saturated hydrocarbons is far more puzzling though it has received much systematic study at higher temperatures (250°C. upwards)[4]. The lower aliphatics through butane appear to degenerate step-wise by the addition of molecular oxygen at the terminal methyl group to form a dihydroxy compound which immediately splits in one of two ways to form the corresponding aldehyde or carbon monoxide, water, or the next lower hydrocarbon. Under severe conditions this new hydrocarbon undergoes the same step-wise degeneration as the original one until formaldehyde, formic acid and ultimately carbon dioxide and water are reached. Superimposed upon this simple scheme are side reactions which lead to the formation of various alcohols, acids, aldehydes, and mixed ketones. For molecules more complex than butane the oxidative degeneration seems to proceed through an aldehyde which is successively broken down, step-wise, to lower aldehydes, acids, carbon dioxide, and water. In a long chain molecule the first point of attack is reported to be the terminal methyl group, or the terminal methyl group of the longest branch of a branched chain compound[5]. Whether this theory for the mechanism of the oxidation of paraffinic hydrocarbons holds for lower temperatures (100° to 200°C.) is unknown and the extremely low rate of action at the lower thermal levels makes study in this region difficult. Since isooctane, the type paraffinic hydrocarbon employed in this work, was stable toward oxygen at 100° for 24 hours, the mechanism of any slight action that may take place is of itself unimportant, but because the oxidation processes of the naphthenic hydrocarbons above 250°C. appear to be paraffinic in nature after fission of the ring, the question of the mechanism of paraffinic degeneration is interesting as it will be shown that certain naphthenes are not entirely stable in the oxygen bomb.

8. The reaction of aromatic hydrocarbons in the higher temperature region is peculiar in that the comparatively stable benzene neucleus yields on fission fragments with an extreme degree of oxidizability, though quite drastic conditions are necessary to rupture the ring of the mother hydrocarbon benzene. When side chains are present, as in a substituted benzene, the

initial point of attack is reported to be the carbon atom farthest removed from the benzene ring. Owing to the rather drastic treatment necessary to convert a typical hydrocarbon of this group, toluene, to benzaldehyde or benzoic acid, it was not believed that the mild conditions employed in the present work would affect the simpler aromatics; but, with the more complex members whose side chains were numerous and complex, the stability of the molecule was suspected to be somewhat lower. In a like manner, the hydrogenated benzenes or naphthenes might parallel, in a qualitative way at least, the behavior of the parent hydrocarbons.

9. Information on the stability of the lower alicyclics of the cyclopentane, cyclobutane and cyclopropane series was quite scanty, although it has been indicated by DuPont[6] that certain alkylated cyclopentanes are slowly attacked by gaseous oxygen. In this report the only members of the alicyclic series considered belong to the cyclohexane and cyclopentane groups, as the lower ring systems have not been positively identified in petroleum.

10. There is general agreement that conjugated and non-conjugated polyolefines, cyclic and non-cyclic monoolefines, in the respective order of activity, are the type hydrocarbons most susceptible to oxidation and notorious for their gum-forming tendencies. The aromatic, naphthenic, and aliphatic types are less reactive and it is of such types that the bulk of aviation gasoline is comprised. However, it should be remembered that most samples of aviation gasoline do contain some unsaturates, generally of the monoolefinic type. While aliphatic monoolefines such as diisobutylene are usually stable under ordinary conditions of storage, though not in the oxygen bomb, it is important to note that certain cyclic olefines and compounds with unsaturated residues attached to a benzenoid ring may be quite the contrary. Numerous such substances occur in the boiling range of aviation base stock and are quite probably present therein. Though the actual percentages of such substances are low, the possibility exists that they, once activated by the absorption of oxygen may be able to induce and promote the absorption of oxygen by those classes of compounds of intermediate stability so that a relatively small amount of active material can catalyze the decomposition of a quantity of ordinary stable matter. The question also arises as to the possibility of the more complex benzenes, naphthenes and other alicyclics acting in a similar manner, since increasing complexity of the molecule seems to confer decreased stability, with the result that the stability characteristics of some certain of these hydrocarbons approach those of the more stable olefines.

(e) <u>Narrative of Original Work Done at this Laboratory</u>

11. In the initial phases of this study a check was made through the scientific literature to find what hydrocarbons had been definitely identified as present in petroleum from which aviation base stocks are derived. Thus, the work could be confined

to such hydrocarbons as are most likely to be encountered in aviation fuels. Though the presence of aromatic hydrocarbons in petroleum has been recognized for three-quarters of a century, only in recent years have definite individuals been identified[7]. Such aromatics as benzene, toluene, the xylenes, pseudo-cumene, para-cymene, diethyl benzene, tetramethyl benzenes, isoamyl benzene, and probably tertiary-butyl benzene, have been isolated from various crudes and are probably contained in all petroleums. Cyclic hydrocarbons with 5, 6, or more carbon atoms to the ring are present in considerable quantities in Russian petroleum and seem to occur constantly in American crudes and the products derived therefrom. The members of the aliphatic group are always present but they are of little interest to this report because of their extreme stability. Olefinic hydrocarbons are not normal constituents of natural petroleums but arise through thermal decomposition during fractionation and cracking. The quantities of such unsaturated material in aviation gasoline are necessarily low, being so kept by the vendor that the product offered can pass the acid heat test of Naval specifications. However, the acid heat test does not exclude unsaturates entirely, as has been shown in Naval Research Laboratory Report No. P-1360. A gasoline may contain relatively high percentages of olefinic matter and still pass the Federal specifications, provided a considerable fraction of the fuel is aromatic in nature. Since, in the cases of some unsaturates, even small amounts may lead to decreased stability of a gasoline blend, it was thought instructive to examine the behavior of selected olefinic hydrocarbons along with the corresponding saturated and benzenoid types. In the appendix, a table will be found summarizing the compositions of typical American petroleum cuts in the aviation gasoline range and specific hydrocarbons that have been isolated and identified therein. From this list was selected the hydrocarbons used in this work supplemented with such other structures as would give some measure of completeness to the range of the investigation.

12. The hydrocarbons so selected were secured either by synthesis at this Laboratory or by careful purification of the best grade of commercial product obtainable; the physical constants, boiling point and refractive index were determined, and such precautions were taken as to insure in all materials a high degree of purity. The individual hydrocarbons were subjected to chemical tests and to ultra-violet and infra-red examination to insure the absence of other types of hydrocarbons or oxygenated bodies. The oxidation experiments were conducted by treating 100 cc of an aromatic or saturated hydrocarbon, or 100 cc of a 10 mol per cent of an unsaturated hydrocarbon in carefully purified isooctane, with oxygen at 100 pounds initial pressure for 24 hours in a bomb immersed in a constant temperature bath set at 100°C. At the end of that time the bombs were cooled, then opened, and a portion of the oxidized hydrocarbon reserved for spectroscopic and chemical analysis. Fifty cubic centimeters of the remainder were evaporated under an air jet at 155°C. for a determination of the gum formed. A data sheet embodying the findings of this work is included in a following

section. Given there also are the details of the work done as well as more elaborate information on the preparation and source of the materials used. In Appendix A will be found matter pertaining to the details of the actual synthetic work performed; Appendix B relates the methods and results of spectroscopic examination.

METHODS

(a) Preparation of Materials

13. All the cyclopentane hydrocarbons with the exception of methyl cyclopentane, which was prepared by the catalytic isomerization of cyclohexane , were made by the vapor phase hydrogenation of the corresponding olefine over nickel powder at 280°C.[9]. The yields were in the neighborhood of 90%, the loss being accounted for as mechanical, except for cyclopentane. In the preparation of this hydrocarbon from cyclopentene, fission of the ring apparently took place with the formation of 25 to 30 per cent normal pentane. The cyclopentenes with the exception of cyclopentene itself were prepared from cyclopentanone (which in turn was derived from the pyrolysis of adipic acid) by condensing the ketone with an appropriate alkyl halide to form the corresponding tertiary alcohol, catalytically dehydrating the alcohol with iodine, drying and distilling the resulting hydrocarbon from sodium. Cyclopentene was made from cyclopentanone by reducing the ketone to the alcohol with nickel in a steel bomb at 150°C. under 1300 pounds hydrogen pressure[9], esterifying the resulting alcohol with hydrobromic acid and eliminating hydrogen bromide from the cyclopentyl bromide with alcoholic potassium hydroxide to give the olefine in the usual fashion. Most of the cyclohexane hydrocarbons were prepared by the liquid phase reduction of the corresponding benzene hydrocarbons under high pressure in a steel bomb with a supported nickel catalyst. The crude products were treated with nitrating acid (one part nitric to two parts sulfuric acid), washed, dried and distilled with sodium. Cyclohexane and methyl cyclohexane were best grade Eastman Kodak products appropriately purified. Benzene, toluene, ethyl benzene, pseudo-cumene, and cymene, which were used as such or in the synthesis of the corresponding cyclohexanes, were Eastman Kodak best grade products purified as described elsewhere. Some of the propyl benzene was prepared from phenyl magnesium bromide and propyl bromide. The yields, however, were so poor that the bulk of this hydrocarbon was synthesized from benzyl magnesium chloride and diethyl sulfate[10]. Isopropenyl benzene resulted in a 55% yield from the action of acetone on phenyl magnesium bromide followed by dehydration of the alcohol formed with 30 per cent sulfuric acid. Styrene was procured from the Eastman Kodak Company and vacuum distilled just before use; tertiary butyl benzene, from the Sharples Corporation. The preparation of propyl cyclohexene was analagous to the preparation of propyl cyclopentene. That is, propyl bromide from normal propyl alcohol was converted to the organo-magnesium derivative which was condensed with cyclohexanone to give the tertiary alcohol. This last yielded the

desired hydrocarbon on catalytic dehydration with iodine. The cyclohexone was made from cyclohexanol by the dehydrogenation of the alcohol over reduced copper at 250 to 330°C. in a hydrogen stream.

(b) Description of Apparatus

14. The steel bombs in which the oxidation experiments were conducted were of such a size as would accommodate an 8-ounce glass oil bottle covered with an inverted 30 cc beaker. They were fitted with flanges through which six symmetrically placed 1/2" cap screws engaged six similar threaded holes in the bomb head. Closure was effected by evenly tightening the bolts so that a lead gasket was compressed between the under-face of the head and the body of the bomb proper. One bomb was equipped with a ground metal joint. In use, it was found that such a closure had a tendency to leak so that it was usually necessary to interpose a very thin lead gasket at the pressure surfaces to insure tightness. Through the center of the head was placed an outlet tube drilled with a 1/8" hole which communicated with the atmosphere and to a high pressure oxygen source through a Hoke valve and through a reducing guage and another valve through 2-1/2 feet of 1/8" copper tubing with a Bourdon tube of a Bristol multiple recording guage. The guage was equipped to measure and record the pressure in the bombs over a period of 24 hours. The bombs were filled at 25°C., being brought to this temperature by immersion for a suitable period in a 25°C. bath. All runs were made in an oil bath maintained at 100 ± .1°C. by means of a bimetallic thermostat actuating a relay on the immersed heated coils. The large volume bath, about 12 gallons of oil, was used so that it would have the capacity of absorbing any sudden large amount of heat that might be generated in the bombs during the oxidation process and also minimize the cooling effect on the bath when the cold bombs were first introduced. Even with a bath of this size during the initial moments, it was necessary to throw in auxiliary heating coils to compensate for the heat capacity of the bombs and contents.

(c) Methods of Analysis

15. The hydrocarbons were all tested for peroxides before and after oxidation with potassium iodide-hydrochloric acid reagent and potassium thiocyanate-ferrous sulfate. Before each test the samples of oxidized hydrocarbons were blown for 15 minutes with a fine stream of nitrogen to sweep out dissolved oxygen. In the case of each reagent the formation of free iodine or the appearance of the red color of ferric thiocyanate within one minute was taken as positive. The tests were controlled by blanks. Aldehydes and alcohols were proved by the formation of the highly colored iron salts of acet-hydroxamic acids under the proper conditions; methyl ketones, by the characteristic color reaction with sodium nitro-prusside; acids, by the decoloration of 1/2000 normal potassium hydroxide-phenolthalein solution. The details of the spectroscopic examinations are described in Appendix B of this report.

For the gum determinations, 50 cc of hydrocarbon were evaporated in a 100 cc tared Berzelius beaker on the standard A.S.T.M. gum bath under a jet calibrated to deliver air at the rate of one liter per second.

(d) Description of Procedure

16. Before all runs the oxygen bombs were carefully cleaned with acetone, thoroughly washed with hot water, rinsed with distilled water, and dried. One hundred cc of the hydrocarbon were measured into a chemically clean 8-ounce oil bottle, the neck of the bottle protected by an inverted 30 cc beaker which allowed free ingress of gas but prevented the entrance of metallic particles or oxide from the bomb walls and head, and the bombs closed. Oxygen was admitted through a reducing valve and, after flushing two times with oxygen to 110 pounds pressure, the bombs were left at 110 pounds pressure for 15 minutes in a bath at 25°C. Thereafter, the pressure was adjusted to exactly 100 pounds guage and the bombs transferred to the 100°C. bath. At the end of 24 hours they were removed, cooled to 25°C., and opened. A portion of the oxidized material was reserved for chemical and spectrographic analysis and 50 cc of the remainder used in the gum determination. The results of chemical tests and the spectrographic information are presented below in tabular form (Table II). Also tabulated are figures on the gum formation, induction periods and pressure drops during oxidation.

17. Before the oxidation experiments were undertaken, exploratory work was done to determine the minimum length of time that certain of the more unstable hydrocarbons would need to be subjected to treatment with oxygen to produce definite alteration and appreciable gum formation. Thus, runs of 1-1/2, 3, and 6 hours were made using 10 mol per cent solutions of diisobutylene, cyclohexene, and 3-methyl cyclohexene in isooctane. At the end of oxidations the bomb contents were examined as described. From these findings which are listed in Table I, it was concluded that representative results could best be obtained by allowing the oxidations to run 24 hours.

18. Because of the reactivity of the olefinic hydrocarbons, all such compounds were oxidized in dilute solutions in isooctane. The pure olefines absorb such large amounts of oxygen and deposit such quantities of gum that comparable results could not be obtained with concentrated solutions. Furthermore, a concentration of 10% unsaturated matter represents the maximum ever likely to be encountered in gasoline blends; hence, the solutions used more nearly approximate the composition of an olefinic fuel than do the pure substances. The dilutions were made on the basis of mol per cent rather than volume per cent, so that equivalent quantities of reactive material would be subjected to test each run.

TABLE I

Compound; 10 Mol % in Isooctane	Time of Oxidation	Pressure Drop #/sq.in.	Gum Mg./100 cc	Oxygenated Compounds*			
				Peroxides	Aldehydes	Acids	Alcohols
Diisobutylene	0 hours (start)	-	0.0	-	-	-	-
	1.5	0	0.0	-	-	-	-
	3.0	< 1	0.4	Trace	-	Trace	-
	6.0	< 2	0.4	+	+	+	+
Cyclohexene	0 hours (start)	-	0.0	-	-	-	-
	1.5	0	0.2	Trace	-	-	-
	3.0	< 1	0.4	+	+	+	+
	6.0	< 2	0.6	+	+	+	+
3-Methyl cyclohexene	0 hours (start)	0	0.0	-	-	-	-
	1.5	0	0.0	Trace	-	-	-
	3.0	< 1	0.6	+	+	+	-
	6.0	< 2	0.6	+	+	+	+

* Legend: (+) = positive; (-) = negative. The tests represent the results of chemical analysis.

Spectrographic analysis confirmed these results (see Appendix B).

TABLE II

RESULTS OF 24-HOUR OXIDATION AT 100 POUNDS OXYGEN PER SQUARE INCH AT 100°C.

Name	Mol % in Isooctane	Induction Period (Hours)	Pressure Drop in #/sq.in.	Milligrams of Gum per 100 cc	Oxygenated Compounds					Indications of Oxidation from Change in Ultra-violet or Infra-red Absorption
					Peroxides	Aldehydes	Methyl Ketones	Acids	Alcohols	
Unsaturated 5-membered ring compounds										
Cyclopentene	10	6	92	1786+	+	+	+	+	–	In all cases examined the spectral characteristics of the oxidized samples differed from that of the pure hydrocarbons; see appendix for discussion.
1-Ethyl cyclopentene	10	2	93	1476+	Not tested					
1-n-Propyl cyclopentene	10	2	96	2176+	+	+	+	+	–	
Saturated 5-membered ring compounds										
Cyclopentane	100	24+	0	0.0	Trace	–	–	–	–	
Methyl cyclopentane	100	24+	0	0.0	Trace	–	–	–	–	
Ethyl cyclopentane	100	11-12	4	0.4	+	–	+	+	–	
n-Propyl cyclopentane	100	14	4	0.2	+	–	+	+	–	
Unsaturated 6-membered ring compounds										
Cyclohexene	10	12	18	29.4	+	+	+	+	Trace	
3-Methyl cyclohexene	10	12	20	5.4	+	+	+	+	Trace	
1-n-Propyl cyclohexene	10	–	54	452.0	Not tested					

(Continued)

TABLE II (Continued)

Name	Mol % in Isooctane	Induction Period (hours)	Pressure Drop in #/sq.in.	Milligrams of Gum per 100 cc	Oxygenated Compounds					Indications of Oxidation from Change in Ultra-violet or Infra-red Absorption
					Peroxides	Aldehydes	Methyl Ketones	Acids	Alcohols	
Saturated 6-membered ring compounds										
Cyclohexane	100	24+	0	0.0	–	–	–	–	–	In all cases examined the spectral characteristics of the oxidized samples differed from that of the pure hydrocarbons; see appendix for discussion.
Methyl cyclohexane	100	24+	0	0.4	Trace	–	–	–	–	
Ethyl cyclohexane	100	16	4	0.4	+	Trace	Trace	–	–	
n-Propyl cyclohexane	100	14	3	0.2	+	Trace	+	+	–	
iso-Propyl cyclohexane	100	14	4	0.0	+	–	+	+	+	
1,2,4-tri-Methyl cyclohexane	100	6	22	0.8	+	–	+	+	+	
1-Methyl, 4-iso-propyl cyclohexane	100	13	8	0.1	+	–	+	+	+	
tert-Butyl cyclohexane	100	20	4	0.0	Trace	–	–	–	–	
Benzenoid Hydrocarbons										
Benzene	100	24+	0	0.0	–	–	–	–	–	
Toluene	100	17	3	0.6	Trace	–	–	–	–	
Ethyl benzene	100	16-17	4	0.4	+	–	Trace	+	–	
n-Propyl benzene	100	9	6	0.0	+	–	+	+	–	
1,2,4-tri-Methyl benzene	100	6	10	1.0	+	–	+	+	+	
1-Methyl, 4-iso-propyl benzene	100	5	22	1.0	+	+	+	+	+	
Diethyl benzene meta- & para-mixture	100		21	6.6	+	+	+	+	+	
tert-Butyl benzene	100	24+	0	0.0	–	–	–	–	–	

(Continued)

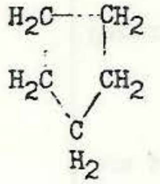
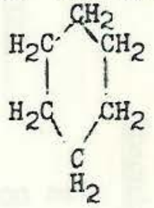
TABLE II (Continued)

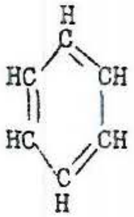
Name	Mol % in Isooctane	Induction Period (hours)	Pressure Drop in #/sq.in.	Milligrams of Gum per 100 cc	Oxygenated Compounds					Indications of Oxidation from Change in Ultra-violet or Infra-red Absorption
					Peroxides	Aldehydes	Methyl Ketones	Acids	Alcohols	
Olefinic Benzenes										
Styrene	10	4	42	256.4	+	+	+	+	+	In all cases examined the spectral characteristics of the oxidized samples differed from that of the pure hydrocarbons; see appendix for discussion.
Allyl benzene	10	24+	0	0.8	+	–	–	+	–	
iso-Propenyl benzene	10	13	2	0.7	+	–	–	+	–	
Aliphatic Unsaturated and Saturated										
Diisobutylene	10	6	11	2.0	+	+	Trace	+	+	
Isooctane	100	24+	0	0.0	–	–	–	–	–	

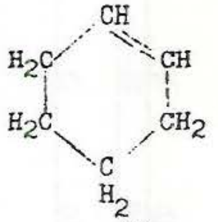
DISCUSSION OF RESULTS

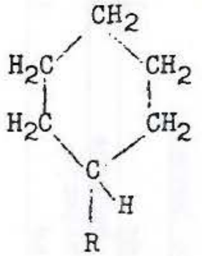
19. The compounds studied included one member each of the aliphatic saturated and monoolefinic series, three cyclopentenes, four cyclopentanes, eight cyclohexanes, three cyclohexenes, seven benzenoid hydrocarbons, and three olefinic benzenes of the styrene series. As was expected, the majority of the olefinic types displayed a marked degree of reactivity with oxygen accompanied by gum formation. The saturated individuals were generally stable in so far as gum formation was concerned, but certain of the more complex naphthenes and complex benzenoids exhibited a tendency to absorb oxygen to yield substances which gave the usual test for peroxidated bodies sometimes accomplished by positive tests for aldehydes, ketones, and acids, though insignificant amounts of gum were formed.

20. It is possible then to classify the hydrocarbons studied into three groups: (1) stable, (2) moderately stable, and (3) unstable. These groupings are shown on the pages immediately following. It will be noted that a representation of the carbon skeleton structure of each hydrocarbon has been given. The symbols

, , , represent , ,

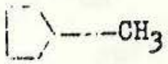
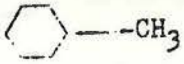
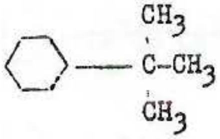
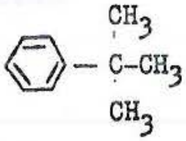
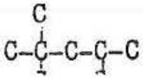
, or cyclopentane, cyclohexane, and benzene respectively.

Similarly, cyclohexene, , is given as 

and  is used for , the derived cyclohexanes.

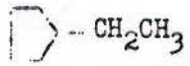
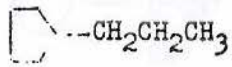
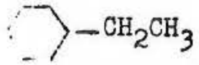
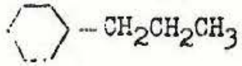
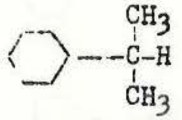
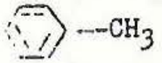
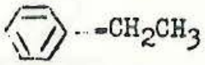
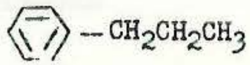
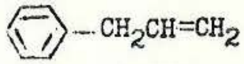
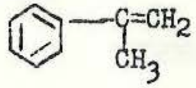
Group 1 (Stable Hydrocarbons)

(a)

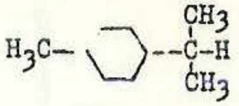
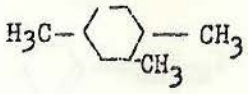
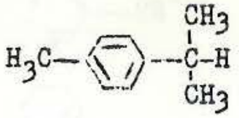
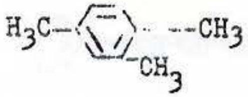
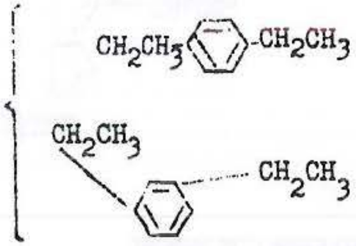
Compound	Structure	Number of Substituent Groups	Mg. Gum per 100 cc	Pressure Drop	Presence of Oxygenated Compounds
Cyclopentane		0	0	0 lbs.	Trace
Methyl cyclopentane		1	0	0	Trace
Cyclohexane		0	0	0	Trace
Methyl cyclohexane		1	0.4	0	Trace
ter-Butyl cyclohexane		1	0	0	Trace
Benzene		0	0	0	Negative
ter-Butyl benzene		1	0	0	Negative
Isooctane	 $\mathrm{C{-}\overset{C}{C}{-}C{-}C{-}C}$	-	0	0	Negative

Group 1 (Stable Hydrocarbons) (Continued)

(b)

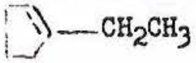
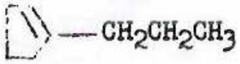
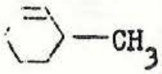
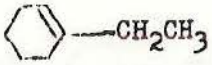
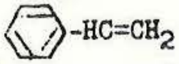
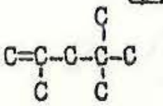
Compound	Structure	Number of Substituent Groups	Mg. Gum per 100 cc	Pressure Drop	Presence of Oxygenated Compounds
Ethyl cyclopentane		1	0.4	4 lbs.	+
Propyl cyclopentane		1	0.2	4	+
Ethyl cyclohexane		1	0.4	4	+
n-Propyl cyclohexane		1	0.2	3	+
iso-Propyl cyclohexane		1	0.0	4	+
Toluene		1	0.6	3	+
Ethyl benzene		1	0.4	4	+
n-Propyl benzene		1	0.0	6	+
Allyl benzene (10 mol %)		1	0.8	0	+
iso-Propenyl benzene (10 mol %)		1	0.7	2	+

Group 2 (Moderately Stable Hydrocarbons)

Compound	Structure	Number of Substituent Groups	Mg. Gum per 100 cc	Pressure Drop	Presence of Oxygenated Compounds
1-Methyl, 4-isopropyl cyclohexane		2	0.1	8 lbs.	+
1,2,4-trimethyl cyclohexane		3	0.8	22	+
1-Methyl, 4-isopropyl benzene		2	0.6	22	+
1,2,4-Trimethyl benzene		3	1.0	10	+
Diethyl benzene* (meta and para mixture)		2	6.0*	21	+

* See next page for footnote.

Group 3 (Unstable Hydrocarbons)

Compound	Structure	Number of Substituent Groups	Mg. Gum per 100 cc	Pressure Drop	Presence of Oxygenated Compounds
Cyclopentene**		0	1786.+	92 lbs.	+
1-Ethyl cyclopentene**		1	1476.+	93	+
1-n-Propyl cyclopentene**		1	2176.+	96	+
Cyclohexene**		0	29.4	18	+
3-Methyl cyclohexene**		1	5.4	20	+
1-n-Propyl cyclohexene**		1	452.0	54	+
Styrene**		1	256.4	42	+
Diisobutylene**		-	2.0	11	+

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* The placement of this compound is problematical. Under a rigid scheme of classification it should be listed with the unstable hydrocarbons. The sample was known to be a mixture of isomers and since it is not at once apparent why at least one of those isomers, 1,4-diethyl benzene, should be more reactive than 1-methyl 4-isopropyl benzene, the liberty is taken of tentatively listing the mixture with those compounds which it most closely resembles in structure. Moreover, the material was used in the pure state in contrast to the hydrocarbons of Group 3 which were blended with an inert diluent.

** Ten mol per cent in isooctane.

Group 3 includes those hydrocarbons which absorbed oxygen during a 24-hour run at 100 pounds and 100°C. and which deposited 10 milligrams or more of gum per 100 cc when the test solution was evaporated at the end of the run. In Group 2 are such compounds as showed an oxygen absorption greater than that represented by a pressure drop of 4 pounds per square inch accomplished by negligible gum formation. Group 1 is comprised of substances in which the treatment with oxygen was accompanied by a drop in pressure of zero to not more than 4 pounds and in which not more than 1 milligram of gum appeared.

21. Group 1 has been divided into sub-groups (a) and (b). The former contains only hydrocarbons which suffered no apparent alteration and showed no oxygen absorption as measured by pressure drops and which contained no oxygenated bodies or only traces of them and which formed no gum. The members in group (b) appeared to be slightly less stable. The justification in listing them thus is that the slight instability they displayed is indicative of a <u>trend</u> toward instability as the complexity of the molecule increases. That this trend is real is borne out in the fact that in all cases where the oxidation was accomplished by a pressure drop, though that drop were small, peroxidic bodies appeared in the treated hydrocarbon and in those cases so examined the spectral characteristics of the treated hydrocarbon differed from that of the original. For example, a decrease in the strength of the sharp C_6H_5 absorption bands was observed in the oxidized sample of 1-methyl-4-isopropyl benzene, where the ultra-violet spectrum of this material was compared with that of the pure untreated compound (see Appendix B, Plate 9). In the cyclohexane series, all the oxidized samples absorbed more strongly in the ultra-violet than did pure materials (see Appendix B, Plate 6). This phenomenon was noted even when there was no evidence of pressure drop but the degree of absorption was greater when a drop in oxygen pressure was discernible on the recording guage. Furthermore, the peroxide tests were generally negative or doubtful in the absence of a pressure drop, but were always positive in the presence of it. Moreover, the indications of the presence of oxygenated bodies became increasingly definite as the pressure drops became more apparent. It will be noted that the saturated parent hydrocarbons of the aliphatic, the benzenoid, cyclopentyl, and cyclohexyl series, were practically non-reactive under the conditions of test. But, as the complexity of the molecules increased evidences of instability began to appear until with two or more substituent groups on the parent nucleus the oxygen absorption rose to such a degree that it is necessary to classify all the poly-substituted cyclic hydrocarbons in the moderately stable class.

22. The compounds of this class are particularly interesting in the light of their pronounced oxygen absorbability on the one hand, and the lack of gumming tendency on the other.

It is suggested that such oxygenated compounds might function as oxygen carriers in gasoline and as such be able to initiate and accelerate the oxidation of other compounds whose stability level is such that they are not ordinarily affected by atmospheric oxygen under the usual conditions of storage. It is known that certain unstable olefines catalyze the oxidation of other bodies. For example, the amount of gum formed from the mixtures of cyclohexene and styrene is several times greater than the gum appearing when equivalent amounts of either substance are oxidized alone. Some of the compounds studied, methyl isopropyl benzene, 1,2,4-trimethyl benzene and its hydrogenated analogue, have oxygen absorptive properties approximating that of a 10 mol per cent solution of cyclohexene in isooctane. Hence, the possibility is suggested that such hydrocarbons may possess catalytic properties. An investigation is in progress to throw more light on the behavior of mixtures.

23. It might be pointed out that the instability of cyclic saturated hydrocarbons and the corresponding benzene derivatives is dependent more on the number of groups substituted on the ring rather than on the complexity of a single group. Thus, normal propyl cyclohexane and normal propyl benzene are stable while 1,2,4-trimethyl cyclohexane and 1,2,4-trimethyl benzene show a decided affinity for oxygen. Again, methyl isopropyl benzene and diethyl benzene with two substituent groups are unstable, while tertiary butyl benzene with one substituent, though of the same molecular weight, appears to rival benzene and toluene in stability.

24. The third group, characterized by compounds of pronounced gumming tendencies and high oxygen absorbability, contains the olefinic analogues of some of the hydrocarbons which have been discussed. Due to the reactivity of these compounds, the oxidation experiments were not run on the pure substances but on 100 cc of a 10 mol per cent of the substance dissolved in isooctane. The following points are of interest: By far the most unstable hydrocarbons were cyclopentene and the substituted cyclopentenes. The consumption of oxygen was practically quantitative, beginning after a short induction period, and gum deposition was about eight times greater than in the case of styrene and 60 times as great as from cyclohexene. Ethyl cyclopentene forms somewhat less gum and propyl cyclopentene somewhat more than cyclopentene itself. The actual figures are of little significance since the results of gum determinations are quite erratic when large amounts are encountered.

25. In the cyclohexene series gumming tendency was increased by the addition of a substituent group, provided attachment of such a group to the ring was to one of the two carbons bearing the double bond. For example, a 10 mol per cent solution of normal propyl cyclohexene furnished about 450 milligrams of gum per 100 cc on 24-hour oxidation as compared with 18 milligrams from 10 mols of

cyclohexene; but, the gum formed from 10 mols of 3-methyl cyclohexene, where the methyl group is not attached to either of the carbons involved in the formation of the ethylenic linkage, was only 5 milligrams per 100 cc. Although the oxygen absorption was equal in this case to that of cyclohexene, it was less than half that of the propyl derivative where the propyl group was on carbon atom #1. It is realized that these two cases are not strictly analagous since the substituent groups were not the same in each instance. However, it is felt that the effect observed is connected more with the position of the group in relation to the double bond than to the nature of the group itself. This effect of position structure on the oxidizability and gumming tendency of olefines will be investigated more thoroughly since it may afford some insight into the instability of the various position isomers of the corresponding saturated analogues.

26. Another point of interest in the cyclopentene oxidation is that the character of the gum forming in those instances differed from that from the cyclohexenes or from diisobutylene in that the gum was of a highly insoluble character. At the end of a run, the bottom of the test bottle was covered with a layer of yellow-orange polymeric product and the supernatant hydrocarbon contained only a fraction of a percentage of the total amount of gum produced. In a case of diisobutylene (2 milligrams of gum), styrene (256 milligrams of gum), and propyl cyclohexene (452 milligrams of gum), all the gum remained in the solution and precipitated only on evaporation of the solvent. Of the cyclopentene gum only 80 milligrams remained in solution, while about 1800 milligrams precipitated. Hydrocarbons which yield such insoluble gums cause trouble in storage because they leave sparingly soluble matter behind to foul the supply lines and tanks of the storage system. The soluble gums, however, will usually appear on the intake ports, carburetor parts, and manifold in motor operation, though they are not apt to be left in the storage system, except in such locations as experience large evaporation losses.

27. The behavior of diisobutylene was especially noteworthy. A 10 mol per cent solution of this material in isooctane deposited only 2 milligrams of gum in the accelerated oxidation test, indicating a remarkable degree of stability which has been borne out in long-time storage tests (see Naval Research Laboratory Report No.P-1481

28. Three other olefines also exhibit a striking degree of resistance to attack by molecular oxygen, namely, 3-methyl cyclohexene, allyl benzene, and isopropenyl benzene. The first of these has been discussed. It was surprising that isopropenyl benzene, or α-methyl styrene, and allyl benzene should be so stable when compared with styrene, to which these compounds are closely related in structure. It should be borne in mind, however, that oxidation experiments were conducted, as in the case of all the olefinic hydrocarbons, on 10 mol per cent solutions of the substance in isooctane. The dilution of a reactive hydrocarbon with a relatively

inert one such as isooctane has a stabilizing influence on the oxidizability in the pressure bomb that transcends the effect that may be ascribed to simple concentration changes alone. In other words, 20, 30, or 40 per cent solutions of a given olefine in an inert solvent when subjected to accelerated oxidation yield not 2, 3, or 4 times as much gum as is obtained from a 10 per cent solution, but generally more. That this stabilizing effect is not a simple function of dilution is shown in the following data on the 24-hour oxidation of varying percentages of diisobutylene and isooctane.

Per Cent in Isooctane	Induction Period* Hours	Gum Mg./100 cc
10	7	2.0
20	4	4.8
30	2-1/3	41.6
40	1-3/4	109.5
50	1-1/2	183.8

Therefore, the unexpected stability of allyl and isopropenyl benzene in 10 per cent solution does not predict that this stability shall persist in more concentrated solutions or with the pure substances; in fact, other investigators[11] have reported that 33 per cent solutions of these hydrocarbons yield considerable amounts of gum on accelerated oxidation. But for the purposes of this report the results are comparable with the data on other olefinic compounds examined since the tests were conducted on solutions containing equivalent concentrations of reactive structures. As such, it is evident that under the conditions of the test, allyl and isopropenyl benzene have stabilities greater than those of any of the olefines examined.

CONCLUSIONS

29. Isooctane and the simpler hydrocarbons of the cyclopentane, cyclo-hexane, and benzenoid series are stable toward oxygen at 100 pounds pressure at 100°C. for 24 hours.

30. As the complexity of the molecule increases in the cyclopentane, cyclohexane, and benzenoid series by the addition of side chains, the oxygen-absorbing properties of the hydrocarbon increase, though the gum formation is low. The effect is noticeable in the di-substituted naphthenes and benzenes and is most pronounced in the tri-substituted compounds of which the 1,2,4-trimethyl member was the most complex investigated. The effect appears to be dependent more upon the number of the substituents rather than on the complexity of a single group, though the isopropyl compounds are slightly less stable than the normal-propyl derivatives.

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* Length of time elapsing before a noticeable drop in pressure occurred.

31. The olefinic hydrocarbons are the least stable of all studied, absorbing oxygen readily and yielding gum in greater or less amounts. The hydrocarbons of the cyclopentene series are the most reactive with oxygen and display the most marked gumming tendencies followed by styrene, the cyclohexene hydrocarbons, and the aliphatic monoolefine diisobutylene in the order of decreasing activity. Generally, the addition of side chains to a cyclic olefine increases the yield of gum, though the effect is determined by the position of the substituent group in relation to the double bond.

RECOMMENDATIONS

32. In order that sufficient data may be accumulated to permit a correlation of the structural characteristics of gasoline hydrocarbons with gumming tendency, and so that some attempt may be made to interpret the results of accelerated oxidation with deterioration on storage, it is recommended:

(a) That this preliminary study be extended to a wider range of compounds, including such substances as seem to hold the key to the problem at the present time.

(b) That the effect of moderately stable hydrocarbons - complex naphthenes, and benzenes - on the stability characteristics of less stable substances such as diisobutylene be investigated.

(c) That certain of the more accessible compounds be stored under conditions likely to be encountered in actual practice and that the behavior of these samples be checked at suitable intervals of time against the results obtained on accelerated oxidation.

(d) That the new fuels called "safety fuels" having a boiling range from 300°-400°F. should be carefully studied as to stability, because it has been shown in this report that the heavier hydrocarbons have a tendency toward instability.

APPENDIX A

Presented below is a table showing the compositions of certain typical petroleum cuts. As has been mentioned earlier, these data are included to show that the pure hydrocarbons selected for oxidation studies are actually present in aviation base stocks.

TABLE A

Hydrocarbons in Typical Cuts of
American Petroleum in the Boiling
Range of Aviation Gasoline.

(a) Percentages of Hydrocarbon Types[12].

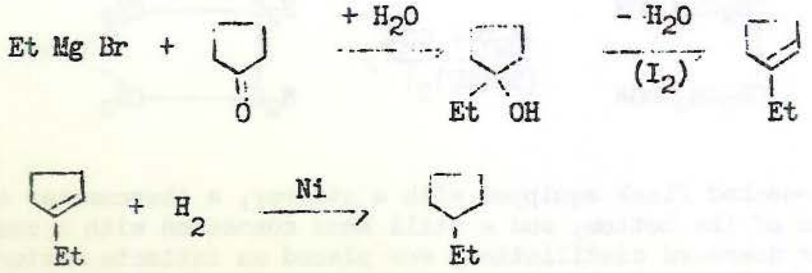
Source	Mexia, Texas			Tonkana, Okla.			Davenport, Okla.			Huntington Beach, Calif.		
Type Structure / Fraction: B.P.°C.	Benzenes	Naphthenes	Paraffins	Benzenes	Naphthenes	Paraffins	Benzenes	Naphthenes	Paraffins	Benzenes	Naphthenes	Paraffins
60-95	29	17	54	6	26	68	5	21	74	4	31	65
95-122	21	22	57	8	34	58	7	28	65	6	48	46
122-150	19	23	58	12	43	45	12	33	55	11	33	55
150-200	16	21	63	20	41	39	16	29	55	17	61	22

(b) Percentages of Individual Hydrocarbons[13].

Isolated from Ponca, Okla. Oil

Naphthenes and Paraffins	Estimated % in 55-180°C.Fraction	Benzenoids	Estimated % i 55-180°Fractio
2,3-Dimethyl butane	0.3	Benzene	0.6
n-Hexane	3.6	Toluene	2.20
2-Methyl hexane	1.8	Allyl benzene	0.20
2,2,3-Trimethyl pentane	0.2	Xylenes	2.10
n-Octane	7.0	1,3,5-Trimethyl benzene	0.3
Methyl cyclopentane	1.45		
Cyclohexane	2.20	1,2,4-Trimethyl benzene	3.0
Dimethyl cyclopentanes	3.20		
Methyl cyclohexane	2.20		
Ethyl cyclopentane	0.30		
Dimethyl cyclohexanes	2.20		
n-Propyl cyclopentane	0.7		
Ethyl cyclohexane	0.7		
1,2,4-Trimethyl cyclohexane	0.7		

Of the hydrocarbons selected from the above list, the majority were synthetically prepared at this Laboratory. In this section are described the details of these syntheses and methods of purification of these and such commercial compounds as were available. In general the synthetic processes were as follows: A ketone containing the desired ring structure was treated with the appropriate magnesium organo-bromide to give a tertiary alcohol which was dehydrated to yield the corresponding olefine. The olefine was then hydrogenated to the saturated analogue. Schematically, using ethyl cyclopentane as an example:



Most of the cyclopentane derivatives were obtained in this manner. The exceptions will be noted elsewhere. The cyclohexane hydrocarbons were mostly prepared by the high pressure hydrogenation of the corresponding benzenoid hydrocarbons. In this series the preparation of methyl cyclohexane from toluene is cited as an example. Most of the benzenoid hydrocarbons were best quality commercial products carefully purified before use. The isooctane and the diisobutylene were Standard Oil Company of New Jersey products. The refining of these materials is described later.

The discussion of the synthetic operations will follow the scheme:

I. PREPARATION OF INTERMEDIATES.

- (a) Preparation of necessary ketones.
- (b) Preparation of alcohols.
- (c) Preparation of bromides.

II. PREPARATION OF HYDROCARBONS.

- (a) Special methods of synthesis.
- (b) Dehydration of alcohols.
- (c) The hydrogenation of -
  - (1) Olefines.
  - (2) Benzenoid hydrocarbons.

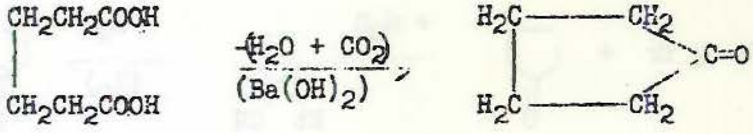
III. PURIFICATION OF COMMERCIAL HYDROCARBONS.

I. PREPARATION OF INTERMEDIATES.

(a) Preparation of necessary ketones.

(1) Cyclopentanone.

Cyclopentanone was prepared by the pyrolytic decarboxylation and the dehydration of adipic acid using barium hydroxide as a catalyst.



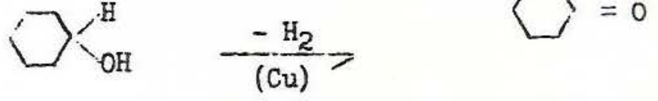
In a 3-necked flask equipped with a stirrer, a thermometer extending to 1 cm of the bottom, and a still head connected with a condenser set for downward distillation, was placed an intimate mixture of 600 grams (4 mols) of adipic acid and 30 grams of barium hydroxide. The flask was heated in a bath of Woods' metal to incipient melting, the stirrer started, and the flask and contents maintained at 285° to 300°C. until only a small residue of about 40 grams remained in the flask which was reserved. The condensate of crude ketone and water was placed in a separatory funnel, the aqueous layer saturated with calcium chloride and withdrawn. The material was dried over night with fused calcium chloride and fractionated twice. The bottoms from the distillation were combined with the residue reserved above and added to the next run. From a series of runs the yields pure cyclopentanone boiling at 128.5 to 130°C. and having a refractive index of 1.4386 at 20° were as follows:

Yield

Run No.	Grams	Per Cent Yield
1	250	77.6
2	288	86.3
3	270	83.9
4	271	84.1
5	275	85.4

(2) Cyclohexanone.

Cyclohexanone was prepared from cyclohexanol by the catalytic dehydrogenation of the alcohol over reduced copper at 320°C. in an atmosphere of hydrogen.



A glass tube 1/2 inch in diameter and 5 feet long was supported at an angle of about 15 degrees from horizontal. The upper end of the tube was packed for about 12 inches of its length with copper oxide held in place with rolls of copper gauze and surrounded by a sand bath which could be heated to the required temperature. To the lower end of the tube was attached an adapter leading to a receiving flask. Between the sand bath and the adapter was arranged a jacket provided with cold circulating water to condense the hot vapors from the catalytic zone. After reducing the copper oxide at 350° in a stream of hydrogen, cyclohexanol was distilled into the tube at a rate of 3 to 4 cc per minute, while maintaining the temperature of the copper between 300 and 350°C. The distillate of the water and crude ketone which collected in the receiving flask was separated, the water discarded, and the ketone recirculated over the copper twice. The condensate so obtained was treated with calcium chloride, dried over night with fused calcium chloride, and fractionated. The yield of the pure material boiling at 166° to 167° at 760 mm with a refractive index of 1.4439 at 20° was 87%.

(b) Preparation of alcohols.

(1) 1-Ethyl cyclopentanol-(1).

In a 5-liter round bottom flask fitted with a stirrer, dropping funnel, and reflux condenser protected with a calcium chloride tube, was placed 150 grams (6.2 atoms) of magnesium turnings, a small crystal of iodine, and 100 cc of a mixture of 654 grams of ethyl bromide in 2 liters of anhydrous ether. As soon as the reaction started 350 cc of ether were added and the remainder of the bromide solution dropped in at such a rate that the ether boiled vigorously. Condensation of the ether was aided by packing the top of the reaction flask with finely cracked ice held in place with a cloth "necktie." The time of addition was 1-1/2 hours or 15 minutes per mol of halide. After the addition of the ethereal solution, the mixture was refluxed on a steam bath for 30 minutes. Thereafter, the percentage of Grignard reagent was determined by differential titration with silver nitrate and nitric acid and found to be 96.5%. Five hundred four (504) grams (6 mols) of dried cyclopentanone and 500 cc of ether were then dropped in at such a rate that the reaction could be controlled. The reaction was very vigorous and required for its completion 2-1/4 hours. The mixture was then refluxed 1/2-hour and tested for the presence of the Grignard reagent with Michler's ketone. The test was negative, indicating that none of the organomagnesium halide survived. After cooling, the ether solution was poured into a 12 liter flask upon a mixture of 400 grams of ammonium chloride and 2000 grams of cracked ice. Ammonium chloride was found to be a much better solvent for the precipitated magnesium hydroxide than mineral acid because the latter tended to cause the elimination of water from the tertiary alcohol even when present in traces. The water layer was separated, extracted with three 200 cc portions of ether, the extracts added to the main portion and the ether distilled through a 30 cm packed column until the temperature of the distilling vapors reached to 50°C. The residue, light brown in color, was then dried over night with 20 grams of anhydrous potassium carbonate and fractionated. The main fraction boiled from 156 to 159°; n_{D}^{20} 1.4528; yield 445 grams, 65%.

(2) <u>1-n-Propyl cyclopentanol-(1)</u>.

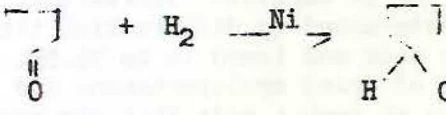
A Grignard reagent of normal propyl bromide (738 grams, 6 mols of halide in 2 liters of ether) was prepared in the usual fashion. Titration of the finished product showed a yield of 98% of propyl magnesium bromide. The time of addition was 15 minutes per mol. To this mixture was added as rapidly as possible 6 mols of dried cyclopentanone. When addition was complete and all the Grignard reagent had been consumed (test with Michler's ketone) the addition product was decomposed as in the above instance. After separating the ethereal layer and distilling the ether, from the residue was obtained a main fraction of 430 grams (56% of theory) boiling at 174 to 177°; n_{D}^{20} ,1.4551.

(3) <u>1-n-Propyl cyclohexanol-(1)</u>.

This alcohol was prepared in a fashion analagous to the above, using cyclohexanone and n-propyl magnesium bromide, yield, 59%; boiling point, 85-89/20 mm; n_{D}^{20} , 1.4638.

(4) <u>Cyclopentanol</u>.

Cyclopentanol was obtained by the high pressure hydrogenation of a portion of the cyclopentanone, the preparation of which has been described.



The apparatus used in this synthesis was designed by the American Instrument Company for high pressure hydrogenations. It consisted of a bomb of chrome-vanadium steel of 3.5 liters capacity closed with a metal head held against a copper gasket by machine bolts. Through the head was a well for a thermocouple and an inlet tube to the hydrogen supply. The system was connected to a pressure guage and through specially constructed valves to a high pressure hydrogen source. The apparatus was mounted in a jacket equipped with heating coils and was so arranged that a rocking motion could be imparted to the bomb and contents. The equipment was tested to withstand working pressures of 20,000 pounds per square inch.

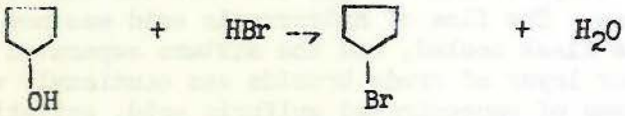
Hydrogenation was accomplished as follows: 840 grams of cyclopentanone (10 mols) were placed in a bomb and the air above the ketone displaced with carbon dioxide. Meanwhile, 15 grams of kieselghur impregnated with 16% nickel as nickel hydroxide was reduced at 450°C. for 2 hours. After cooling, the catalyst was transferred in a hydrogen stream to the cyclopentanone in the bomb, the bomb closed, placed in its cradle, the hydrogen supply attached, and the bomb flushed 3 times with hydrogen to 500 pounds pressure. Thereafter the pressure was built up to 1800 pounds, the rocker started, and the temperature gradually raised to 150° and maintained for 5 hours. On cooling, it was calculated from the drop in pressure that the cyclopentanone had taken up the theoretical amount of hydrogen for conversion to the alcohol. The crude alcohol was washed with a little saturated sodium bisulfite, twice with water, dried over potassium carbonate and distilled. From 10 mols of starting material 835 grams of alcohol, or 94.7%, were obtained. Boiling point 140° to 142°C.; refractive index n_D^{20} 1.4539. This alcohol was used in the preparation of cyclopentyl bromide from which cyclopentene was made as described elsewhere.

(5) <u>Cyclohexanol</u>.

Cyclohexanol was an Eastman Kodak product purified by drying with potassium carbonate and fractionation; boiling point, 161-162°C.; n_D^{20}, 1.4645.

(c) <u>Preparation of bromides</u>.

(1) <u>Cyclopentyl bromide</u>.



Six mols of cyclopentanol were placed in a 2 liter 3-necked flask and treated with anhydrous hydrobromic acid which was prepared by direct union of its elements as described in detail in the preparation of n-propyl bromide. The rate at which the hydrobromic acid was bubbled into the alcohol was so regulated that the action was complete in 6 hours. The crude bromide-hydrobromic acid mixture was transferred to a separatory funnel, the lower aqueous hydrobromic acid solution withdrawn, and the bromide washed cautiously with 100 grams of concentrated sulfuric acid. This washing was performed as quickly as possible since the acid allowed to remain in contact with the material too long causes excessive charring. The washed bromide was then treated once with water, once with dilute sodium carbonate, followed by water until the washings were neutral to litmus. After drying with a small amount of calcium chloride the crude material was fractionated through an efficient column. Yield of two runs, 1251.6 grams or 70 per cent; n_D^{20} 1.4862, boiling point, 137-140°C.

(2) Cyclohexyl bromide.

The preparation of bromcyclohexane from cyclohexanol paralleled that of cyclopentyl bromide; yield, 76%; boiling point, 163-166°; $n\frac{20}{D}$, 1.4948.

(3) n-Propyl bromide.

n-Propyl bromide was made by the action of anhydrous hydrobromic acid on freshly distilled Eastman Kodak Company n-propyl alcohol. The hydrobromic acid was generated by the direct union of hydrogen and bromine. This was accomplished by bubbling a dried stream of hydrogen through bromine heated to 37°C. At this temperature the vapor pressure of bromine is slightly less than 1/2 an atmosphere so that approximately equal volumes of hydrogen and bromine appear in the effluent gas. This gas was lead into a quartz tube heated to redness, next through a column of copper turnings to remove unreacted bromine, and finally was passed into the reaction chamber containing the n-propyl alcohol. The reaction chamber consisted of a 3-necked 2-liter round-bottomed flask fitted with a thermometer that reached nearly to the bottom, a reflux condenser, and a bubbling tube. After 8 mols of propyl alcohol had been placed in the flask it was heated to 95°C. and anhydrous hydrobromic acid containing only a slight excess of hydrogen was admitted through the bubbling tube. The unreacted gases were passed out through the condenser and led beneath the surface of water contained in an Erlenmeyer flask placed on a balance pan. The treatment with hydrobromic acid was continued until this flask began to gain rapidly in weight, indicating that the propyl alcohol was completely saturated with the gas and that the reaction was drawing to a close. The flow of hydrobromic acid was now discontinued, the flask cooled, and the mixture separated under a hood. The upper layer of crude bromide was cautiously washed with 1/3 its volume of concentrated sulfuric acid, agitating the mixture thoroughly to insure the complete removal of the unreacted alcohol. This sulfuric acid wash was followed by water, 10% sodium carbonate, and water again, until the washings were neutral. After drying and fractionating the yield of material boiling from 69 to 71° was 522 grams or 53% of theoretical. Since the yield was low, a second run was made using the standard sulfuric acid in hydrobromic acid method. The hydrobromic acid solution was prepared by the reduction of 1 kilogram of bromine with gaseous sulfur dioxide in the presence of 1 kilogram of cracked ice. Ten mols of n-propyl alcohol were added, the flask attached to a reflux condenser, and 1 kilogram of concentrated sulfuric acid added through a separatory funnel. The mixture was now heated for 3 hours, a condenser set for downward distillation substituted for the reflux, and the mixture slowly distilled until no oily drops were observed in the water at the condenser tip. The crude bromide was separated from the water, washed and dried, and fractionated. Yield, n-propyl bromide, 94%; boiling point, 71-71.2; $n\frac{20}{D}$, 1.4339.

(4) Allyl bromide.

In a 5 liter round-bottomed flask the hydrobromic acid solution was prepared by the sulfur dioxide reduction of 6 mols of bromine and the presence of a liter of ice water. To this was added 770 cc of commercial allyl alcohol which contained 8 mols of pure allyl alcohol. To the flask was fitted a mechanical stirrer, separatory funnel, and a condenser set for downward distillation. The stirrer was started and 600 grams of concentrated sulfuric acid were added gradually through the separatory funnel to the warm solution. Aided by the application of external heat the allyl bromide distilled completely in about 2 hours. The crude bromide was washed with dilute sodium carbonate, dried with calcium chloride, and distilled. Eight hundred ninety five (895) grams (92%) of material boiling at 69 to 72° were obtained, $n\frac{20}{D}$, 1.4657.

II. PREPARATION OF HYDROCARBONS.

(a) Special methods of synthesis.

(1) Cyclopentene.

A 1 liter 3-necked flask which was to serve as a reaction vessel was equipped with a stirrer, a 250 cc dropping funnel, a still head fitted with a thermometer, and a long efficient condenser set for downward distillation. The condenser was attached to a flask which opened to the atmosphere through a trap cooled with an alcohol-solid carbon dioxide mixture. The reaction flask rested on a hot plate controlled with a rheostat. Into it was placed a solution of 3.6 mols of potassium hydroxide in 95% ethanol. This mixture was heated to about 50°C., the stirrer started, and 3 mols of cyclopentyl bromide were dropped in at a rate of 5 to 10 cc per minute. The rate of dropping and the temperature of the hot plate was so controlled that the thermometer measuring the temperature exit vapors did not rise about 60° until the end of the operation. When all the cyclopentyl bromide had been added, the temperature was allowed to reach the boiling point of ethyl alcohol and 75 cc more of distillate was collected at this point. The receiving flask was removed, thoroughly chilled, its contents transferred to a cold separatory funnel, and washed 3 times with iced water to extract the alcohol. Thereafter, the material was carefully dried over solid potassium hydroxide and distilled from sodium. There was practically no forerun; the main fraction boiled at 40 to 44°, and the residue remaining in the flask had a boiling point and physical constants corresponding to ethyl cyclopentyl ether. The main fraction was again distilled from sodium. Boiling point, 44.1°C., index of refraction, $\frac{20}{D}$, 1.4428. The distillate was free of halogens and peroxides and weighed 164 grams, or 80% of theory.

(2) Methyl cyclopentane.

Methyl cyclopentane was achieved by the isomerization of cyclohexane as described by Nenitzescu and Cantuniara[8]. In a liter flask were placed 1-1/2 mols of anhydrous aluminum chloride and 3 cc of water. To this mixture was added 1 liter of cyclohexane and refluxed on a water bath for 6 hours. At the end of this time the hydrocarbon layer was decanted from the aluminum halide, 1000 cc of fresh cyclohexane added, and refluxed as before. The treated hydrocarbon was carefully fractionated through a 5-foot packed column and all the material boiling up to 76° was collected. The residue in the flask was returned to the aluminum chloride, after the second portion of cyclohexane had been decanted, and then the process repeated until approximately 500 cc of the fraction boiling from 69 to 76° had been collected from about 2500 cc of cyclohexane. This material was washed with nitrating acid, then with water, dried over potassium hydroxide and fractionated 4 times from metallic sodium. On the final fractionation 110 grams of material boiling at 71.6 to 72.4° with a refractive index of good agreement with that reported for methyl cyclopentane was obtained.

(3) n-Propyl benzene.

In a dry 5 liter flask equipped with a mercury sealed stirrer and a 1 liter dropping funnel, and a wide bore long upright condenser protected at the top with a calcium chloride tube, was placed 4 mols of magnesium turnings and 2400 cc of dry ether, a small crystal of iodine, and about 50 cc of a solution of 4 mols of freshly distilled benzyl chloride in 1-1/2 liters of dry ether. No difficulty was experienced in starting the reaction. The top of the flask was cooled with cracked ice while the rest of the benzyl chloride solution was dropped in at such a rate that the ether ran in a steady stream from the tip of the condenser. The time of addition was 65 minutes. After all the halide had been added, the mixture was refluxed for 30 minutes and the amount of Grignard reagent was determined by differential titration with standardized nitric acid and silver nitrate, using methyl orange and dichlorofluorescein as indicators, respectively. A 97% yield of magnesium benzyl chloride was obtained. To the Grignard reagent were added 8 mols of freshly distilled ethyl sulfate, the addition being accomplished at such a rate that the mixture boiled continuously. By a careful cooling it was possible to complete the addition in two hours at the end of which time a negative test was obtained with Michler's ketone. The addition product was decomposed with ice water, the precipitated basic salts of magnesium dissolved in the requisite quantity of sulfuric acid, and the hydrocarbon-ether layer separated. Following distillation of the ether, the crude material was boiled with 1 liter of 10% sodium hydroxide for 1 hour to hydrolyze any unreacted ethyl sulfate and water was added to throw the hydrocarbon from solution. After separating and drying the crude material, it was purified by two distillations from sodium. The yield of the second run made as described above was subsequently converted into propyl cyclohexane. The yield of n-propyl benzene (average) was 72%.

(4) Allyl benzene.

Allyl benzene resulted from the interaction of phenyl magnesium bromide with the dry allyl bromide. The Grignard reagent was prepared in the usual fashion from 5 mols of bromobenzene using 6 mols of ether per mol of halide as a diluent. Titration of the Grignard reagent indicated a 95% yield. A solution of 5 mols allyl bromide and one liter of ether was added through a dropping funnel and the mixture refluxed until all the magnesium organo-halide had been consumed. The solution was poured on ice, magnesium hydroxide dissolved in a slight excess of hydrochloric acid and the hydrocarbon isolated by a distillation of the ether and fractionation of the crude product. Calcium chloride was used as a drying agent and distillation from sodium was omitted since strong alkalies cause a shifting of the double bond along the side chain toward the phenyl group. Yield, 60%.

(5) Iso-propenyl benzene.

Iso-propenyl benzene resulted in good yields by the action of dry acetone in dry ether solution upon phenyl magnesium bromide prepared as indicated above. The crude secondary alcohol, 2-phenyl propanol-(2), was dehydrated by refluxing for 3 hours with 30% sulfuric acid. After separation of the acid layer and washing with water, the hydrocarbon was purified as in the case of allyl benzene. Yield, 55%.

(b) Dehydration of alcohols.

(1) 1-Ethyl cyclopentene.

3.75 mols of 1-ethyl cyclopentanol-(1) were placed in a 500 cc round-bottomed flask along with 1 gram of iodine and the mixture distilled slowly through a 30 cm column. The distillate was transferred to a separatory funnel, the aqueous layer withdrawn, and crude hydrocarbon redistilled from 1/2 gram of iodine as above. On this second distillation only a small quantity of water was formed. The water was separated, the hydrocarbon washed with 40% potassium hydroxide, and dried over solid potassium hydroxide. It was then refluxed one hour with sodium metal, cooled, and filtered from the sludge formed, and distilled from fresh sodium. After three distillations a main fraction of 288 grams, or 80%, was obtained. The product was free of halogens, peroxides, and other oxygenated compounds and had a refractive index of 1.4430.

(2) 1-n-Propyl cyclopentene and 1-n-propyl cyclohexene.

1-n-Propyl cyclopentene and 1-n-propyl cyclohexene were obtained in a similar way by the catalytic dehydration of the appropriate tertiary alcohols with iodine.

(c) Hydrogenation of olefines.

(1) Cyclopentane, ethyl cyclopentane, n-propyl cyclopentane.

One hundred sixty (160) grams of cyclopentene, the preparation of which has been described, was hydrogenated in the vapor phase over reduced nickel. This was accomplished by bubbling hydrogen through cyclopentene and conducting the hydrogen saturated with hydrocarbon vapor over the catalyst heated to 250° to 280°C. The temperature of the liquid cyclopentene and the rate of hydrogen flow were so controlled that 20 to 30 cc of hydrocarbon passed over the catalyst each hour. The vapors were collected by passage through a condenser cooled with ice water in a flask immersed in cracked ice and salt which opened to the atmosphere through a solid carbon dioxide-alcohol trap protected with a drying tube. It was necessary to recycle the first distillate since reduction was incomplete as shown by the presence of unsaturates when a test was made with bromine water. The weight of the crude distillate was 158 grams or 96.3% of theory. However, when the material was fractionated only 118 grams of cyclopentene were obtained and about 36 grams of a lower boiling hydrocarbon which had the same boiling point and refractive index as n-pentane. Thus, the vapor phase hydrogenation of cyclopentene is accompanied by ring splitting with the formation of 20 to 25 per cent of n-pentane. It is of interest to note that no evidence of the opening of the ring occurred when ethyl cyclopentene was similarly reduced. The yield of the ethyl cyclopentane from 1-1/2 mols of ethyl cyclopentene was 95%, the loss being accounted for as mechanical since no trace of cyclopentane which might result from the splitting of an ethyl group nor any hexane was found. The same was true of n-propyl cyclopentane in which synthesis a yield of 96% of pure hydrocarbon was obtained by 2 cycles of the corresponding olefine over nickel in a hydrogen stream.

Ethyl cyclopentane and propyl cyclopentane were prepared from the corresponding olefines following the same method as described for cyclopentane.

(d) Hydrogenation of benzenoid to cyclohexanoid hydrocarbons.

The preparation of all the cyclohexane hydrocarbons, with the exception of cyclohexane itself, depended upon the high pressure hydrogenation of the corresponding aromatic compound. Methyl cyclohexane from toluene is given as an example: Four mols of toluene were placed in the hydrogenation apparatus which has already been described (see the reduction of cyclopentanone to cyclopentanol). Ten grams of catalyst (2-1/2 grams per mol) were reduced in hydrogen at 400°C. for 2 hours, cooled, and transferred to the toluene in a stream of carbon dioxide. The catalyst was prepared according to the method of Adkins. Briefly, 58 grams of c.p. nickel nitrate hexahydrate in 80 cc of distilled water were ground for an hour with 50 grams of kieselghur which had been previously digested and washed with nitric acid. At the end of this time the mixture was homogeneous and flowed as freely as heavy lubricating oil. It was then poured slowly into a solution of 38 grams of ammonium carbonate and 200 cc of distilled water. The mixture was filtered at suction, washed with several 100 cc portions of water and dried over night. An accurately weighed sample of the material was leached with hot nitric acid, filtered in a Gooch crucible, washed thoroughly, and the nickel content of the combined washings and nitric acid extract determined in the usual fashion by precipitation of the metal with dimethylgyloxime. The amount of nickel so determined was 16%.

After the reduced catalyst had been transferred to the toluene the bomb was closed, flushed three times with hydrogen, and then filled with hydrogen to 1800 pounds initial pressure at room temperature. Shaking was started and the temperature of the bomb slowly increased to 150 to 200°C. (The simpler benzene derivatives usually reduced between 150 and 175°; the more complex ones required the higher temperature.) In the case of the present preparation the reduction of toluene began at 155° and was complete within 15 minutes. After cooling, the material was removed from the bomb, washed with nitrating acid, dried, and distilled twice from sodium metal. The crude yield was quantitative.

Ethyl, n-propyl, iso-propyl, 1-methyl 4-iso-propyl, tert-butyl, and 1,2,4-trimethyl cyclohexane were prepared as indicated above by the hydrogenation of the appropriate benzenoid hydrocarbons. As in the case of toluene, the reduction was complete and the yields approached quantitative as shown by a complete failure of any of the hydrogenated materials to react in the slightest degree with nitrating acid. Ethyl, and tertiary-butyl benzene required from 1/2 to 1 hour for complete reduction. But in the reduction of the propyl, iso-propyl, and 1-methyl 4-iso-propyl derivatives, the action was not complete until 5 hours had elapsed.

III. PURIFICATION OF COMMERCIAL HYDROCARBONS.

(1) Cyclohexane.

The material was Eastman Kodak Company product purified as follows: 500 cc of hydrocarbon were washed three times with nitrating acid, twice with concentrated sulfuric acid, and once with potassium hydroxide, dried over solid potassium hydroxide, and distilled twice from sodium metal. A middle fraction of 300 grams was taken for this work.

(2) Cyclohexene.

Commercial cyclohexene was shaken three times with 100 cc portions of saturated ferrous sulfate in sulfuric acid (0.5%), followed by steam distillation from a solution made alkaline with caustic potash. The distillate was dried, refluxed over sodium, cooled, and after allowing the sludge to settle, the hydrocarbon was decanted onto fresh sodium metal in a clean flask and redistilled from sodium ribbon twice. The middle fraction of the distillate taken for study was free of peroxides and other oxygenated bodies and had a refractive index that agreed well with the values reported in the literature. 3-Methyl cyclohexene was similarly purified to yield a product which had the following constants: boiling point, 102.5 to 102.8, $n \frac{20}{D}$, 1.4418.

(3) Benzene and toluene.

One thousand (1000) grams of the hydrocarbons were purified by three washings with 50 cc of cold concentrated sulfuric acid, followed by washing with water, 30% potassium hydroxide, and then with water again. The hydrocarbons were dried for several hours over calcium chloride, allowed to stand over night over phosphorous pentoxide, filtered into a clean flask containing sodium ribbon, and distilled from sodium twice. The middle fractions were taken.

(4) Ethyl benzene, iso-propyl benzene, 1-methyl 4-iso-propyl benzene, 1,2,4-trimethyl benzene, and tertiary-butyl benzene were washed once with 50 cc of concentrated sulfuric acid, followed by three washings of 100 cc each of 85% acid. Thereafter the purification process paralleled that of benzene and toluene.

(5) Diisobutylene.

Five gallons of commercial diisobutylene from the Standard Oil Company of New Jersey were distilled through a 5-foot column and the fraction with the boiling point between 100-104°C. was shaken with 30% potassium hydroxide, dried over potassium hydroxide, and refractionated twice, only the middle fraction (boiling between 102.3 and 103°C.) of the final distillation being reserved. The distillate was free of peroxides.

(6) Iso-octane.

Five gallons of commercial iso-octane were washed successively three times with concentrated sulfuric acid, twice with 5% oleum, and then alternately three times with nitrating acid and concentrated sulfuric acid. Following the acid treatments the nitro- bodies were removed from the hydrocarbon by treatment with 30% caustic followed by a thorough washing with water. Three distillations from sodium metal gave a metal fraction with a boiling point of 99.5-101°C. The material was shown to be free of unsaturates, aromatic material, and oxygenated bodies, by both chemical tests and spectroscopic examination. From its refractive index the hydrocarbon seemed to be a mixture of 2,2,4-trimethyl pentane with isomeric octanes. Assuming that only 2,2,4- and 2,2,3-trimethyl pentane are present in the material, the iso-octane contains about 90% of the former to 10% of the latter.

TABLE B

PHYSICAL CONSTANTS OF HYDROCARBONS

Name	Boiling Point;760 mm/corr.			Refractive Index at 20°, d line	
	Determined NRL	Value from Literature		Determined NRL	Value from Literature**
Cyclopentanes					
Cyclopentane	49.3	50 49.4	(12)* (13)	1.4060	1.4039 (12)* 1.4070 (13)
Methyl cyclopentane	71.6-72.4	71.8 71.9	(12) (13)	1.4104	1.4099 (13)
Ethyl cyclopentane	103.3	103	(14)	1.4198	1.4201 (13)
n-Propyl cyclopentane	130.4-130.8	130.6 131.3	(13) (14)	1.4262	1.4269 (13)
Cyclopentenes					
Cyclopentene	44.1	44.5 46.0	(13) (15)	1.4228	1.4262 (13) 1.4207 (15)
1-Ethyl cyclopentene	107.1-108	106.5 108.0	(13) (16)	1.4430	1.4411 (13) 1.443- (16)
1-n-Propyl cyclopentene	130.7-131.7	131.7	(13)	1.4453	1.4435 (13)
Cyclohexanes					
Cyclohexane	80.6	80.8	(14)	1.4260	1.4273 (14) 1.4254 (13)
Methyl cyclohexane	100.7	100.8 101.0	(14) (13)	1.4229	1.4235 (14) 1.4254 (13)
Ethyl cyclohexane	131.6	131.6 131.9	(13) (14)	1.4330	1.4320 (13)

* Literature reference; see Bibliography.
** Corrected to 20°C. where necessary.

(Continued)

TABLE B (Continued)

Name	Boiling Point; 760 mm/corr. Determined NRL	Boiling Point; 760 mm/corr. Value from Literature	Refractive Index at 20° d line Determined NRL	Refractive Index at 20° d line Value from Literature**
n-Propyl cyclohexane	156.6	155.7 (13)* 149.5 (12)	1.4370	1.4360 (13)*
iso-Propyl cyclohexane	154.2	150 (12) 150-153 (17)	1.4409	
1,2,4-Trimethyl cyclohexane	144-146	143-4 (14)	1.4325	1.429- (14) 1.4320 (18) 1.4331 (18)
tert-Butyl cyclohexane	171.3	166-7 (16)	1.4464	
1-Methyl 4-iso-propyl cyclohexane	171.3-171.6	170 (12)	1.4402	1.437- (12) 1.4393 (19) 1.4515 (19)
Cyclohexenes				
Cyclohexene	82.9	83 (12)	1.4463	1.4461 (12)
3-Methyl cyclohexene	102.5-102.8	103 (12)	1.4418	1.443- (12)
n-Propyl cyclohexene	155.5-155.8	154-155 (20)	1.4573	1.4576 (21)
Benzenes				
Benzene	80.1	80.08 (15) 80.4 (13)	1.5010	1.5016 (15) 1.4995 (13)
Toluene	110.5	110.5 (12) 110.4 (13)	1.4964	1.4962 (12) 1.4947 (13)
Ethyl benzene	136.1	136.1 (21)	1.4952	1.4958 (21)
n-Propyl benzene	159.6-160.6	159.4 (21) 158.6 (13)	1.4934	1.4925 (15)
iso-Propyl benzene	153	152-3 (21)	1.4930	1.4923 (21)

* Literature reference; see Bibliography.
** Corrected to 20°C. where necessary.

(Continued)

TABLE B (Continued)

Name	Boiling Point; 760 mm/corr. Determined NRL	Boiling Point; 760 mm/corr. Value from Literature	Refractive Index at 20° d line Determined NRL	Refractive Index at 20° d line Value from Literature**
1,2,4-Trimethyl benzene	169.2-170	169.2 (14)	1.5049	1.5051 (14)
tert-Butyl benzene	168.9	168.7 (21)	1.4924	1.4963 (21)
Diethyl benzene (meta- and para-mixture)	180.0-182	182,183 (12, 15)	1.4957	1.4955 (12,15)
1-Methyl-4-isopropyl benzene	177.0	177 (15)	1.4907	1.4904 (13)
Olefinic Benzenes				
Styrene	48-50/20 mm	----	1.5447	1.5443 (22)
Allyl benzene	60-61/20 mm	----	1.5136	1.5143 (23)
Iso-propenyl benzene	64-65/20 mm	----	1.5358	1.5366 (24)
Aliphatics				
Iso-octane***	99.5-101	99.3 (25)	1.3927	1.3916 (25)
Diisobutylene	102.3-103	102.6 (21)	1.4095	1.4082 (26)

* Literature reference; see Bibliography.

** Corrected to 20°C. where necessary.

*** Approximate composition: 10% 2,2,3-trimethyl pentane; 90% 2,2,4-trimethyl pentane.

APPENDIX B

INFRA-RED AND ULTRA-VIOLET ABSORPTION MEASUREMENTS

I. INTRODUCTION.

Infra-red and ultra-violet absorption measurements have been made on some of the compounds discussed in the preceding pages. The absorption spectra in either the ultra-violet (2000-3000 angstrom units) or the near infra-red (1-10μ) were determined for each compound so investigated before and after oxygenation for various time intervals at 100°C. and 100 pounds per square inch. Marked differences between two such spectra often occur, providing information of two-fold usefulness: (1) Minute chemical changes, as weak oxidation of a hydrocarbon, may give rise to marked variations in the light absorbing properties which thus serve as a delicate index of whether a reaction has occurred; (2) the nature of the new absorption spectrum may provide identification of the functional groups present in the reaction product. The ultra-violet absorption, which is generally strong, is more useful in the first of these capacities; the infra-red absorption, which presents the aspect of several discrete bands, each determined by the natural relative frequency of vibration of two atoms or groups of atoms, is of greater value in the second.

Absorption measurements were not made on all the compounds investigated. The time requirements for quantitative spectroscopic measurements, although not inordinate, are such that in this investigation it would have been difficult to keep pace with the march of chemical events. Absorption spectra of any compound were made immediately after oxidation so that no doubt might exist that only reactions occurring in the bomb were under observation.

II. DISCUSSION OF RESULTS.

(a) Diisobutylene.

The infra-red transmission spectrum of diisobutylene (Curve a) and diisobutylene after oxidation at 100°C. and at a starting pressure of 100 pounds per square inch for 3 hours (Curve b) and 6 hours (Curve c) are shown in Plate 1. The thickness of the absorbing layer was 0.01 centimeter.

The following details of these spectra are significant:

1. In the 3μ region a weak band appears in Curves b and c in the position proper to absorption by the -OH group. The weak intensity of this band is characteristic of aldehydes and ketones. Water and alcohol show strong absorption in this region.

2. A very strong band is developed in the oxidized samples at 5.85μ. This absorption band arises from vibration of the C=O group. The strength of the C=O absorption is so strong as to mask the weak band at 5.7μ in pure diisobutylene (Curve a), although it is possible that as a result of oxidation the molecular structure has changed in such a way as to remove the source of the 5.7μ band or to render it inactive. The low dispersion of the spectrometer does not permit definite determination of this question.

3. The C=C vibration band at 6.1μ is present in all three spectra, but the apparent strength of the absorption is greater in the oxidized samples than in pure diisobutylene, the minimum transmission factor being 40% for Curve a, 30% for Curve b, and 20% for Curve c. This increase in band strength could result from an increase in the number of C=C bonds, or from molecular rearrangement with concomitant increase in electric moment or transition probability.

4. Bending vibrations of the CH_2 and CH_3 groups give rise to absorption bands at 6.8μ and 7.2μ. These bands are well resolved in Curve a; they are just resolved in Curves b and c, where the CH_3 band, at 7.2μ in Curve a, appears to be shifted toward longer wave length. It is probable that new unresolved bands appear in the oxidation product in positions overlapping the 7μ bands of pure diisobutylene.* Ketones and aldehydes possess CH_2 and CH_3 absorption bands at slightly longer wave length than the corresponding bands in pure hydrocarbons.

5. New unresolved bands appear in Curves b and c between 8 and 8.5μ, in the domain of absorption by single bonds, presumably C-O in this case. Identification of absorption bands in this region is difficult because the position of the bands are more dependent upon molecular structure than are the bands at shorter wave length. In a mixture of compounds such as the reaction product in this case must be, any allocation of absorption bands in the 8 to 10μ region to particular structural groups may be purely conjectural.

10% (mol) Diisobutylene in Isooctane.

The results displayed in Plate 1 relate to pure diisobutylene and its oxidation products. The specific research with which this report deals was carried out with 10% diisobutylene in isooctane. Infra-red absorption measurements were made for this mixture only in the 6μ region with the purpose of observing whether C=O absorption

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* A similar effect has been observed in the absorption spectrum of the gum formed upon oxidation of cyclopentene. The positions of the bands in the gum were 7μ and 7.4μ, while the unoxidized solution showed bands at 6.8μ and 7.3μ. These results are to be discussed in a subsequent report dealing more specifically with the chemical structure of gums.

would appear before incipience of pressure drop in the bomb. The results are given in Plate 2. It is clear that no trace of increased absorption at 5.85μ exists until the 24-hour sample, for which the pressure drop was 11 pounds per square inch, is reached. Visual inspection of ultra-violet spectra of samples of diisobutylene in isooctane showed no increase in absorption over that produced by the double bond for oxygenation periods of 3 and 6 hours. The 24-hour sample absorbed strongly.

Cyclohexene

Ten mol per cent 3-methyl cyclohexene in isooctane was examined in the 6μ region where, as in the case of diisobutylene, no significant changes in absorption occurred until after an induction period. The results appear in Plate 3. The samples of 0, 3, and 6 hour oxygenation show only the C=C vibration band at 6.1μ. The 24-hour sample has a new band at 6μ which apparently does not result from the presence of a C=O group, the absorption by which is usually at shorter wave length than 6μ.

Absorption spectra, previously obtained, of fresh cyclohexene and cyclohexene that had stood in a stoppered bottle for two years are instructive in connection with the oxidation of this compound. They are given in Plate 4. The interesting features of Curve b, for aged cyclohexene, are the very strong OH absorption band at 3μ, the strong band at 6μ, which overlaps the C=C band of the parent compound at 6.1μ, the slight shift in position of the band near 3μ, and the development of a new band at 9.3μ.

Strong OH absorption at 3μ is characteristic of alcohols and water, while water also absorbs at 6μ.

The bands at 8 and 9.3μ in the oxidized sample are difficult of allocation. Acids[27] often absorb at 8μ, but they also possess a strong C=O band at 5.85μ which is absent here, nor do acids absorb at 3μ. Primary alcohols absorb at about 9.6μ[28], this band shifting successively to shorter wave length in secondary and tertiary alcohols. Secondary and tertiary alcohols absorb near 8μ. Water[29] shows no discrete bands in the region 7-9μ.

In recapitulation, the 3μ OH band common to water and alcohols; the 6μ band, probably due to water; the 8μ and 9.3μ bands, which may well be due to alcohols, taken together with the absence of a C=O band at 5.85μ, indicate, but do not prove, the existence of a mixture of alcohol and water in oxidized cyclohexene. It must be kept in mind that the 8μ and 9.3μ bands may result from peroxide structure.

It is noted in passing that if the predominant structure in oxidized cyclohexene be of alcohol type, then the opinion of Lecompte[29] that the 7μ absorption band should be attributed to the carbon-chain rather than to the alcohol functional group is essentially substantiated in that the strong CH_2 band of cyclohexene at about 7μ suffers no modification upon oxidation of the compound.

Cyclohexanes

Members of the cyclohexane series through 1-methyl 4-isopropyl cyclohexane were examined in the 6μ region before and after 24-hour oxygenation. No significant alterations in infra-red absorption upon oxygenation of any member of the series were observed. The curves are not reproduced here, with one exception. Among the cyclohexanes investigated spectroscopically, the oxidation of 1-methyl 4-isopropyl cyclohexane induced a considerable pressure drop (8 pounds per square inch; gum 0.1 milligram per 100 cc). Therefore, the infra-red spectra from 3 to 10μ of this member and its oxidation product were examined. The results appear in Plate 5; it is apparent that no informative differences between the two exist.

Upon resorting to quantitative measurement of the ultraviolet absorption by these compounds, however, the somewhat surprising result obtained that in every case the oxygenated sample absorbed more strongly than the pure compound, even in cases where no pressure drop during oxygenation had been observed. Curves, representing absorption coefficient plotted against wave length, are shown in Plates 6 and 7. The absorption coefficient, k, is defined by the relation,

$$I = I_o \, 10^{-kt}$$

where I_o and I represent incident and transmitted light intensities and t is the cell thickness in centimeters. Through n-propyl cyclohexane (Plate 6) no notable dependence on structural complexity is apparent in the observed increase in absorption. The results for isopropyl and 1-methyl 4-isopropyl cyclohexane, however, indicate increasing absorption of the oxidized component with greater complexity of the parent compound.

The data of Plates 6 and 7 were derived, for each compound, from pairs of spectra photographed side by side on the same photographic plate, the one spectrum being of the parent compound and the other of the oxidized sample. In some cases two or more sets of spectra were obtained. These were in all cases consistent with each other. The results shown in Plates 6 and 7 are real, even though the absorption coefficients (and their increments in the oxidized samples) are relatively small. The functional group giving rise to this absorption is not established by either the infra-red or the ultra-violet spectra.

Cyclopentanes

Ultra-violet absorption spectra were determined for cyclopentane and methyl- and ethyl-cyclopentane. The measured absorption coefficients are given in Plate 8. No increase in absorption obtained for cyclopentane. Methyl- and ethyl-cyclopentane absorbed more light after oxidation.

In view of the behavior of the cyclohexanes in the infra-red, where no detectable differences between the oxidized and unoxidized samples existed, the cyclopentanes were not examined in that spectral region.

1-Methyl 4-Isopropyl Benzene

Only the most complex benzene was measured in the ultra-violet. The oxidized and unoxidized samples were diluted to 1% (mol) in isooctane. The absorption curves are shown in Plate 9. They show a decrease in strength of absorption of the sharp C_6H_5 bands in the oxidized sample. This effect has been observed by Ramart-Lucas[31] when the C_6H_5 nucleus is joined to the rest of the molecule by an oxygen atom.

The same effect has been consistently observed in this Laboratory in the case of oxidation of commercial gasolines containing aromatics.

III. EXPERIMENTAL.

Infra-red absorption measurements were made with a small (Hilger) rock salt prism spectrometer. Transmission curves were obtained by plotting as ordinates the ratio of the galvanometer deflection with the absorbing cell in the light path to the deflection with the absorbing cell removed.

Reference to a detailed description of the absorption cell has been given, and the cell has been illustrated in an earlier report[32]. The cell thickness required is of the order of 10^{-2} centimeters.

Ultra-violet absorption spectra were photographed with a Gaertner 121-A quartz spectrograph. A low voltage hot cathode hydrogen arc giving a continuous spectrum served as source. When quantitative data were desired, the plates were calibrated by photographing the spectrum of the arc through wire screens of known transmission factors. The data were then reduced by the usual densitometric measurements. In many cases, however, it is sufficient to know that the reaction product absorbs more or less light than the parent compound. In this event the observation is simply made by photographing side by side on one plate the absorption spectra of the parent compound and the reaction product and examining them visually.

Absorption cells for the ultra-violet were conveniently formed by closing the ground ends of glass cylinders of proper length by crystal quartz plates held on with rubber bands. Such a cell is filled by placing one carefully cleaned quartz plate on the clean surface of a table, placing the glass separator ring on that, and pouring in the liquid to the top level of the ring. The second quartz plate is then easily slid into place. The entire assembly can be lifted from the table, and while the opposing quartz windows are held securely between the thumb and forefinger of one hand, the rubber bands are applied with the other. The windows are then scrubbed with lens paper or absorbent cotton slightly wet with acetone to remove finger prints (or rubber finger tips may be worn). If the ends of the glass separator ring have been carefully ground, such a cell will not leak, and it offers the advantage of flexibility in that one pair of windows may be used for absorption cells of any thickness, whereas cells of fixed length with fused on windows must be available in several lengths and micrometer cells of variable thickness are inordinately expensive.

Glass separator rings of 1 mm thickness can be cut from glass tubing. If thinner cells are required (for highly absorbing liquids) thin foil separators may be used. The quartz windows are then squeezed tight against the foil by metal paper clamps or clothes pins.

Many of the ultra-violet measurements reported here were made with cells of 0.2 cm thickness.

IV. SUMMARY AND CONCLUSIONS.

The spectroscopic observations discussed in Section II indicate the utility of ultra-violet absorption measurements in detecting minute chemical changes, since in certain instances increased ultra-violet absorption resulted from oxygenation, even when no pressure drop was observed during the oxygenation period. When such observations need not be quantitative, they may be rapidly carried out.

When gross changes in structure occur, as in the cases of diisobutylene and cyclohexene, the infra-red absorption spectrum proves of value in identifying fairly rapidly functional groups present in the reaction products.

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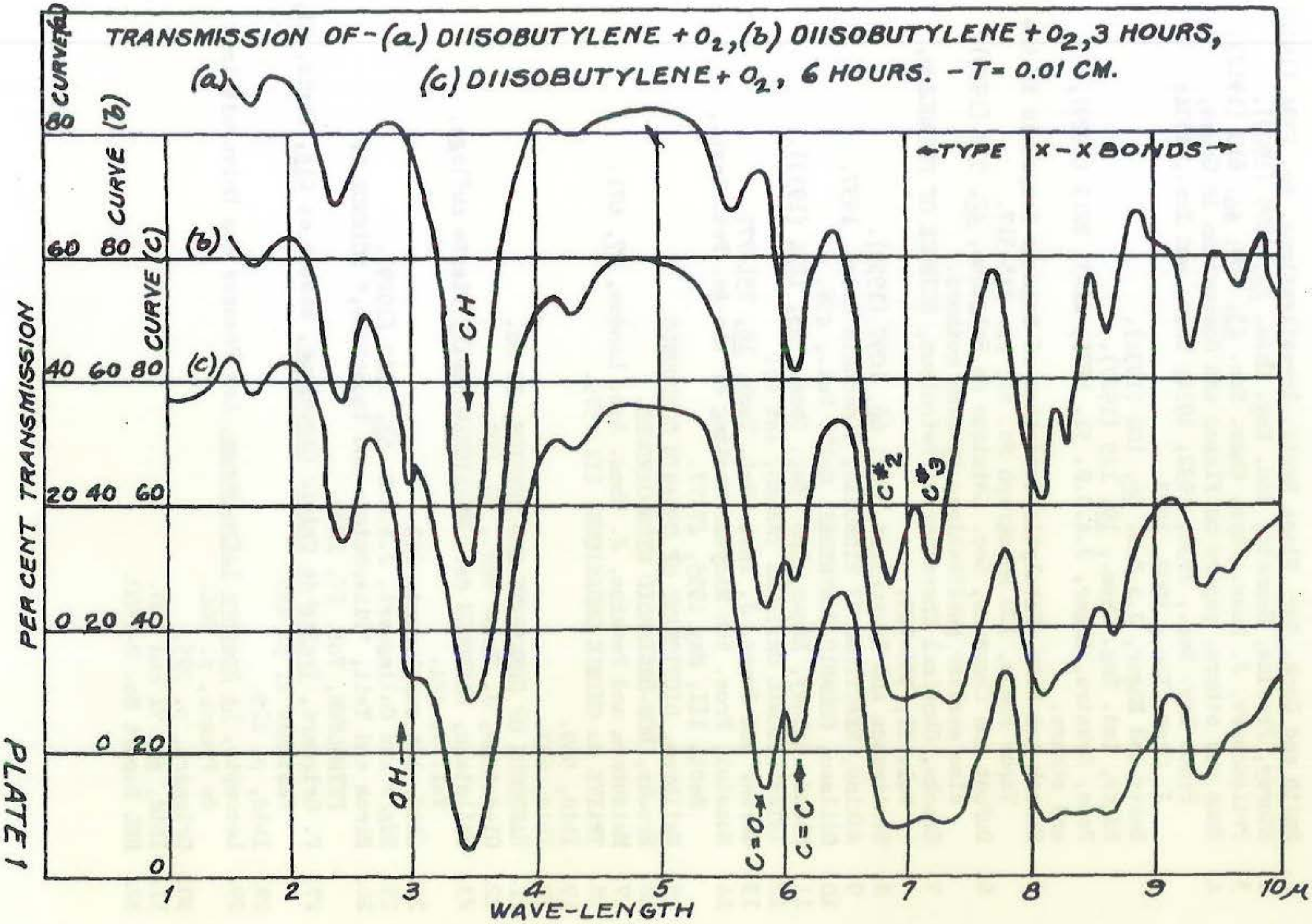

TRANSMISSION OF -(a) DIISOBUTYLENE + O_2, (b) DIISOBUTYLENE + O_2, 3 HOURS, (c) DIISOBUTYLENE + O_2, 6 HOURS. - T = 0.01 CM.

PLATE 1

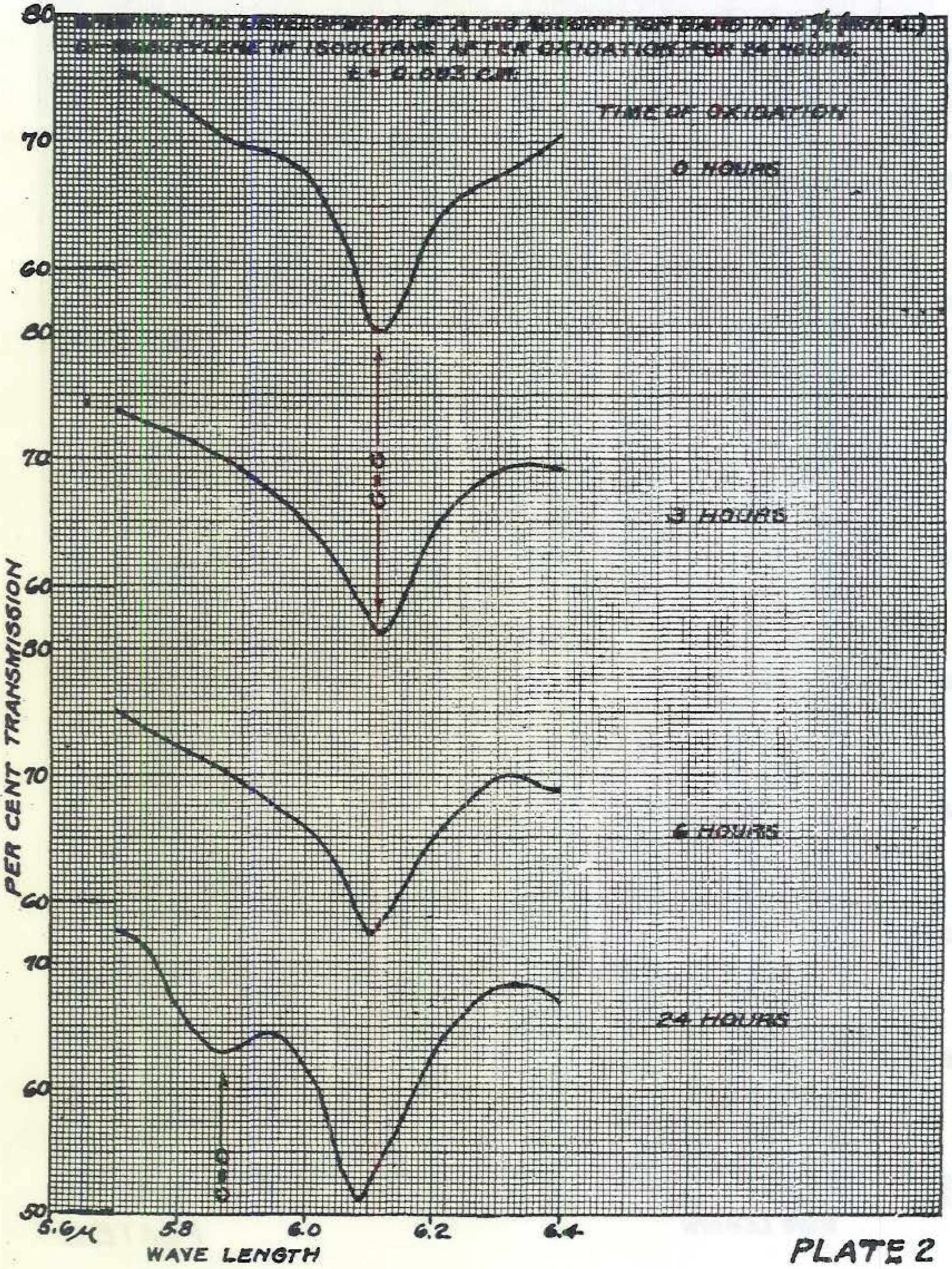
[illegible] THE DEVELOPMENT OF A C=O ABSORPTION BAND IN 10 % (BY VOL.)
[illegible] OF ISOOCTANE AFTER OXIDATION FOR 24 HOURS.
ℓ = 0.083 CM.
TIME OF OXIDATION
0 HOURS
3 HOURS
6 HOURS
24 HOURS
C=O
C=O
80
70
60
50
70
60
50
70
60
70
60
50
PER CENT TRANSMISSION
5.6μ
5.8
6.0
6.2
6.4
WAVE LENGTH

PLATE 2

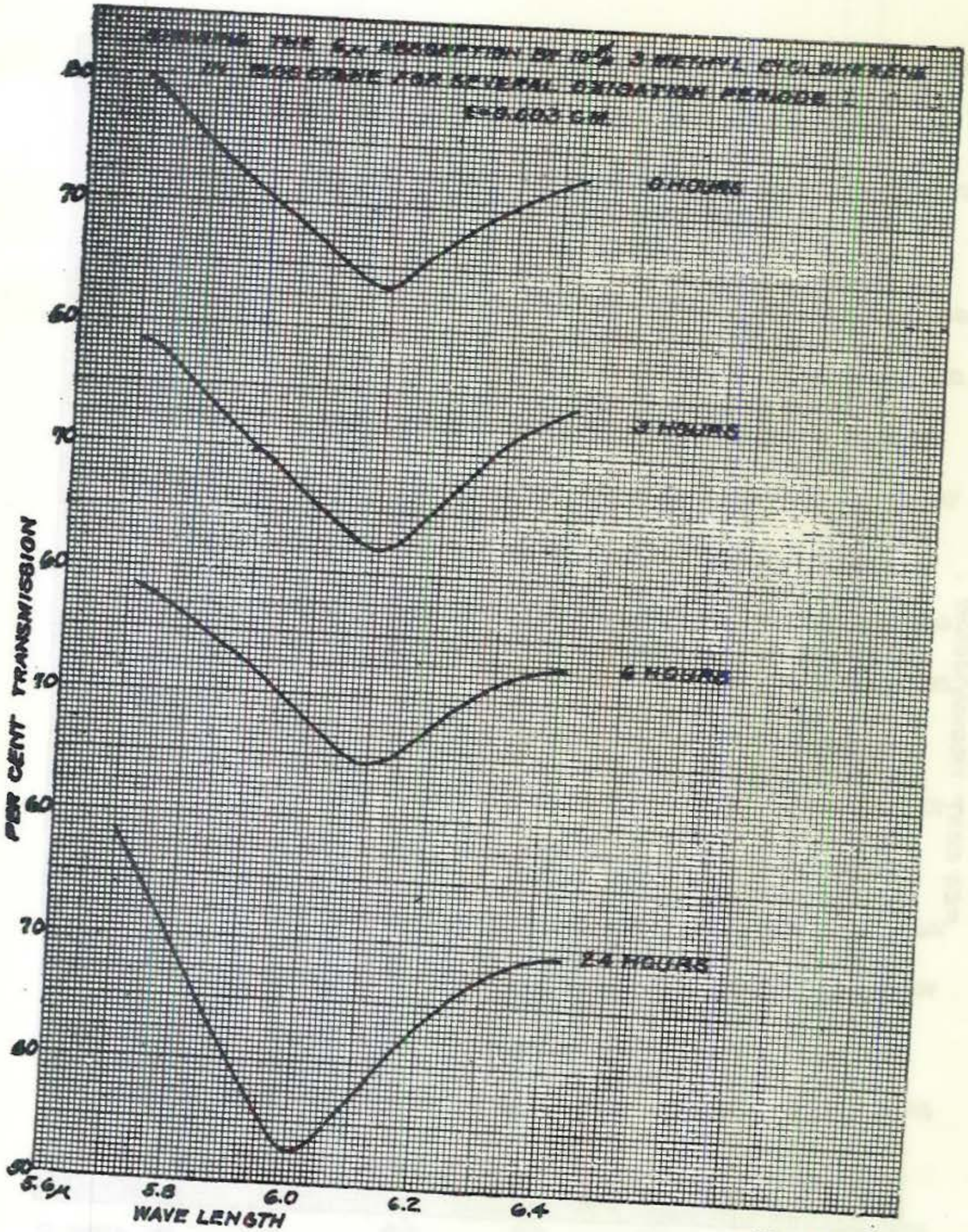
SHOWING THE 6μ ABSORPTION BY 10% 3 METHYL CYCLOHEXENE
IN ISOOCTANE FOR SEVERAL OXIDATION PERIODS.
t=0.003 CM.
0 HOURS
3 HOURS
6 HOURS
24 HOURS
PER CENT TRANSMISSION
80
70
60
70
60
70
60
70
60
50
5.6μ
5.8
6.0
6.2
6.4
WAVE LENGTH

PLATE 3

TRANSMISSION OF-(a) CYCLOHEXENE, (b) CYCLOHEXENE, OXIDIZED

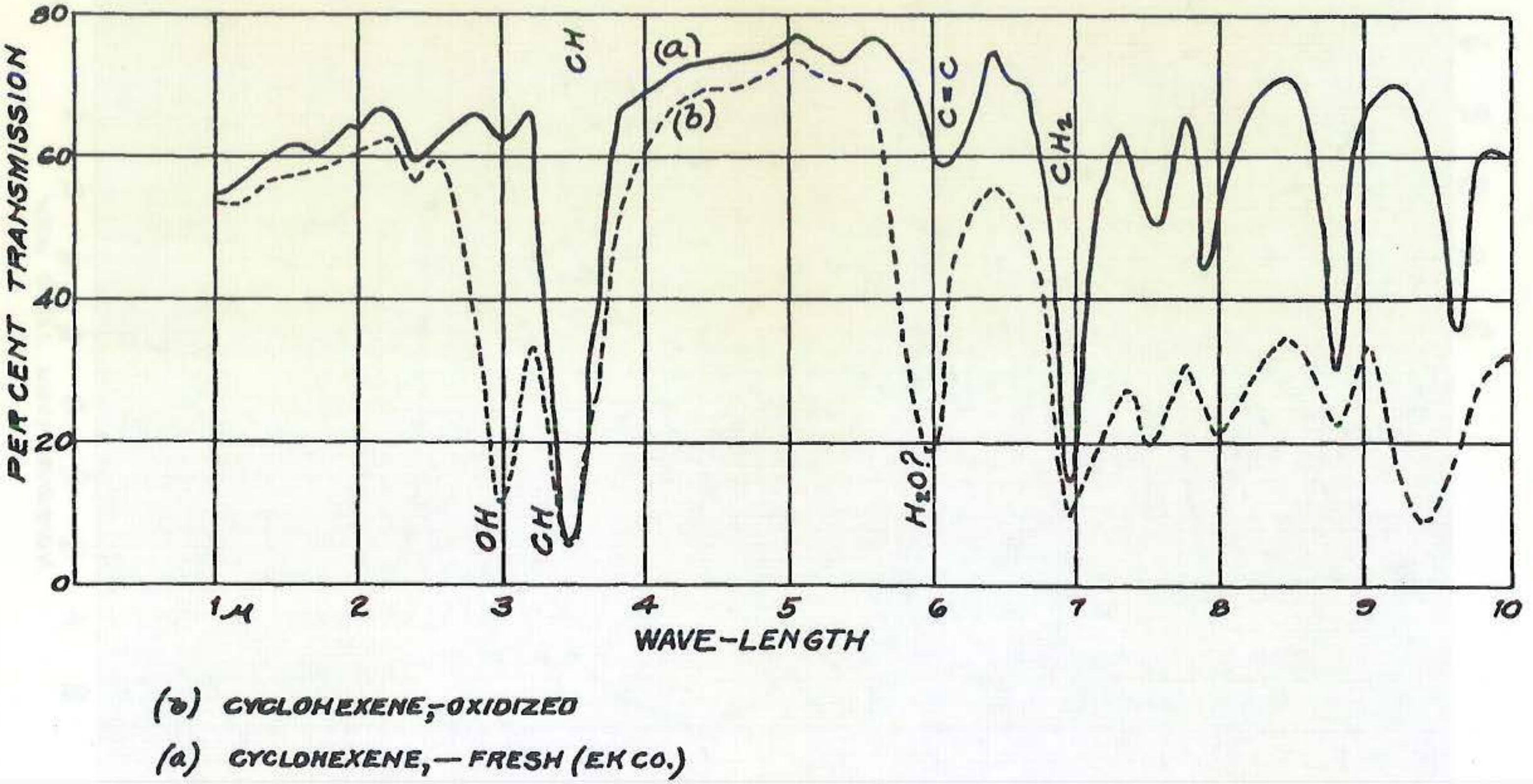

PLATE 4

INFRA-RED ABSORPTION BY 10 % (MOLAL) 1-METHYL-4 ISOPROPYL CYCLOHEXANE IN ISOOCTANE-(a) BEFORE, AND (b) AFTER 24 HOUR OXIDATION.

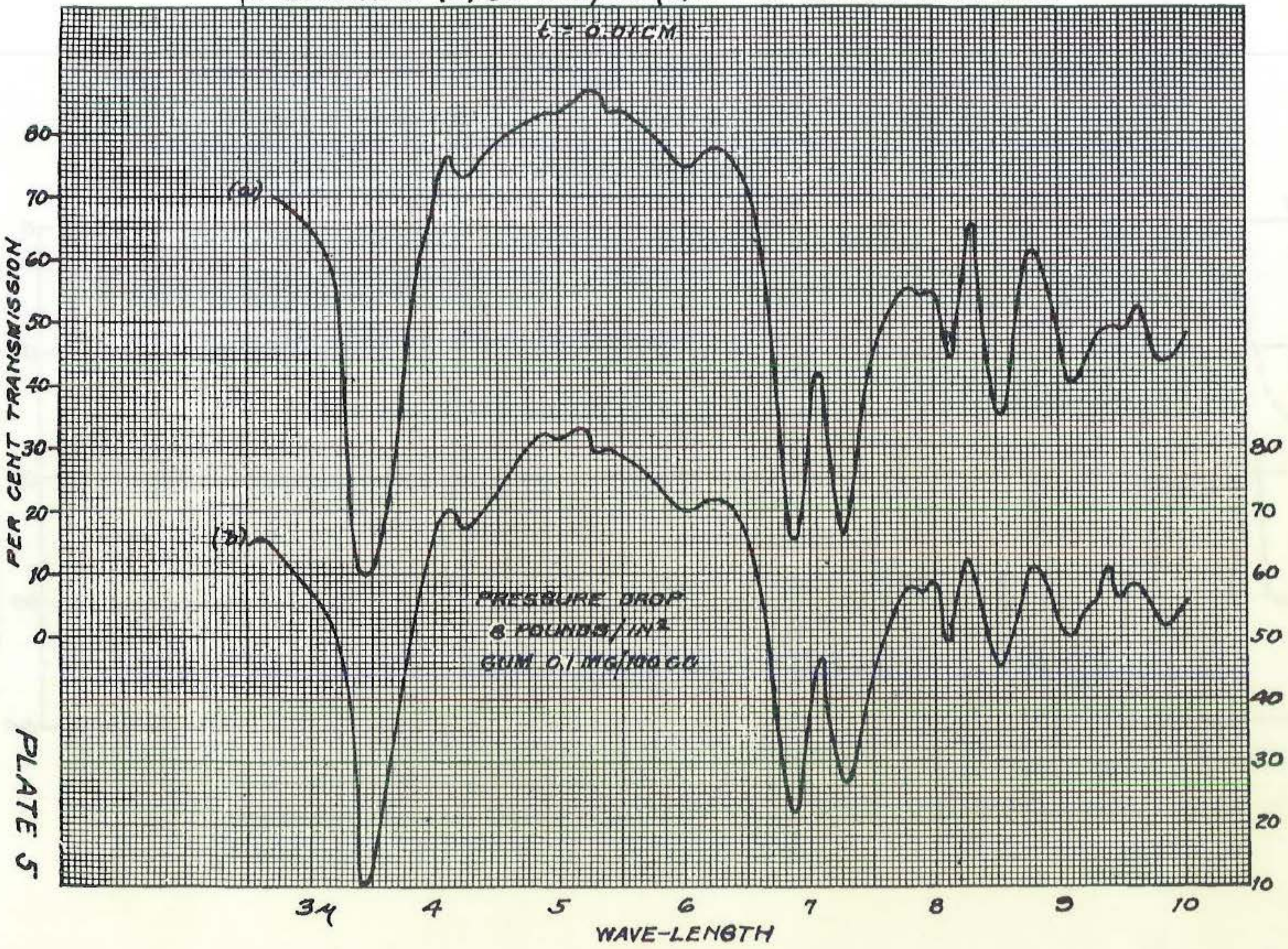

PLATE 5

ULTRA-VIOLET ABSORPTION BY CYCLOHEXANES— (a) BEFORE, AND (b) AFTER, 24 HOUR OXIDATION.

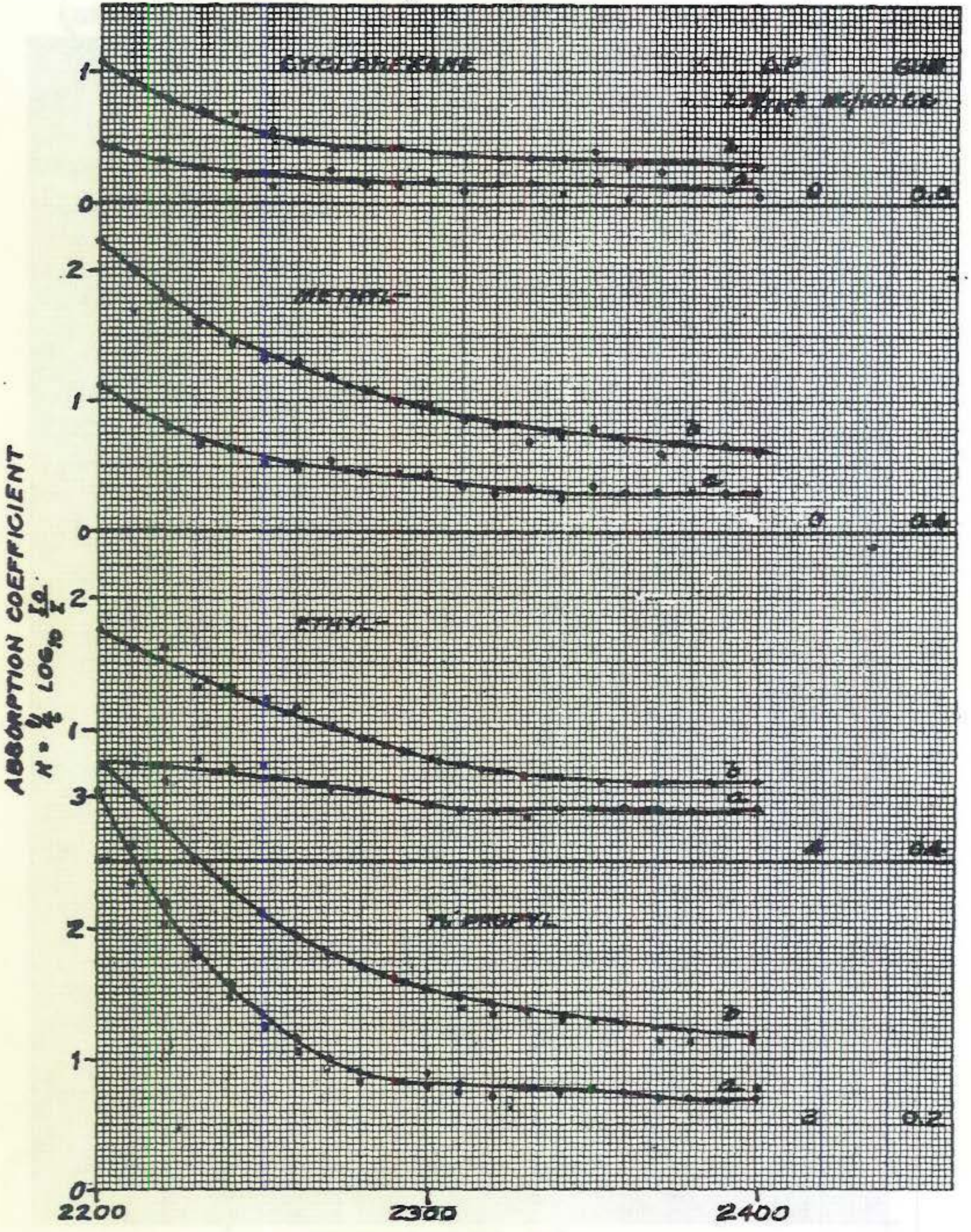

PLATE 6

ULTRA-VIOLET ABSORPTION BY CYCLOHEXANES (CONTINUED)

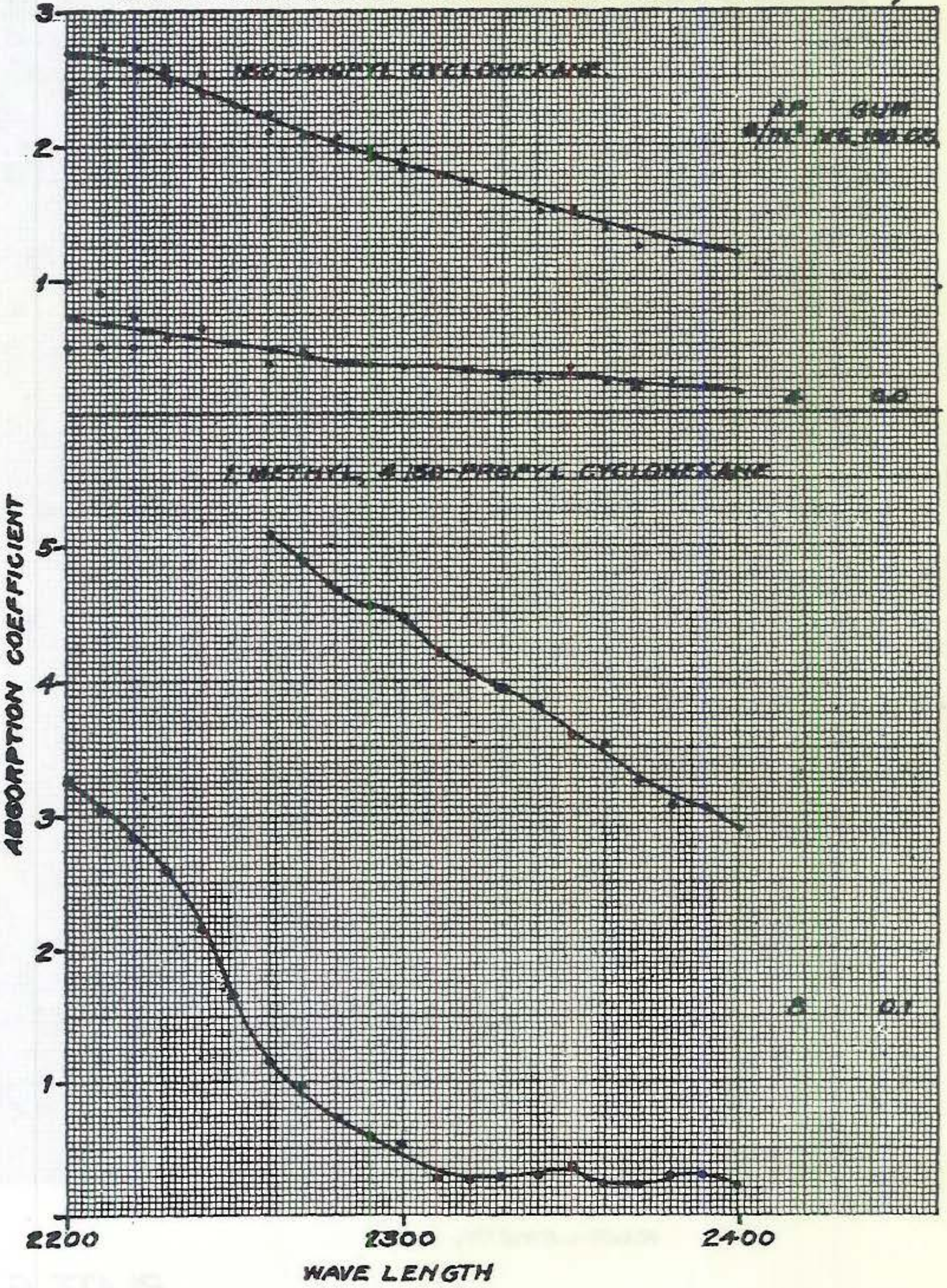

PLATE 7

ULTRA-VIOLET ABSORPTION BY CYCLOPENTANES
(a) BEFORE OXIDATION-(b) AFTER OXIDATION.

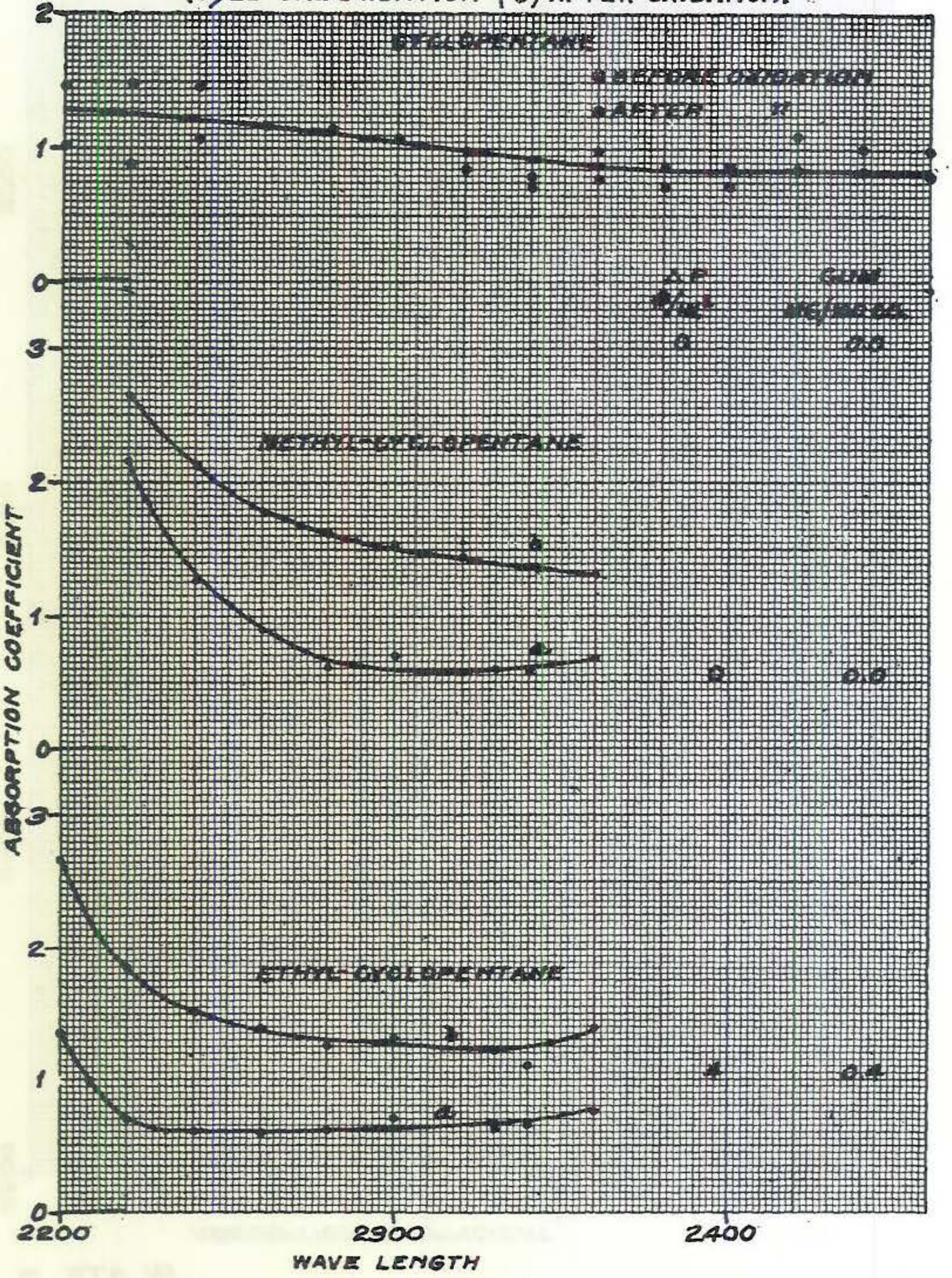

PLATE 8

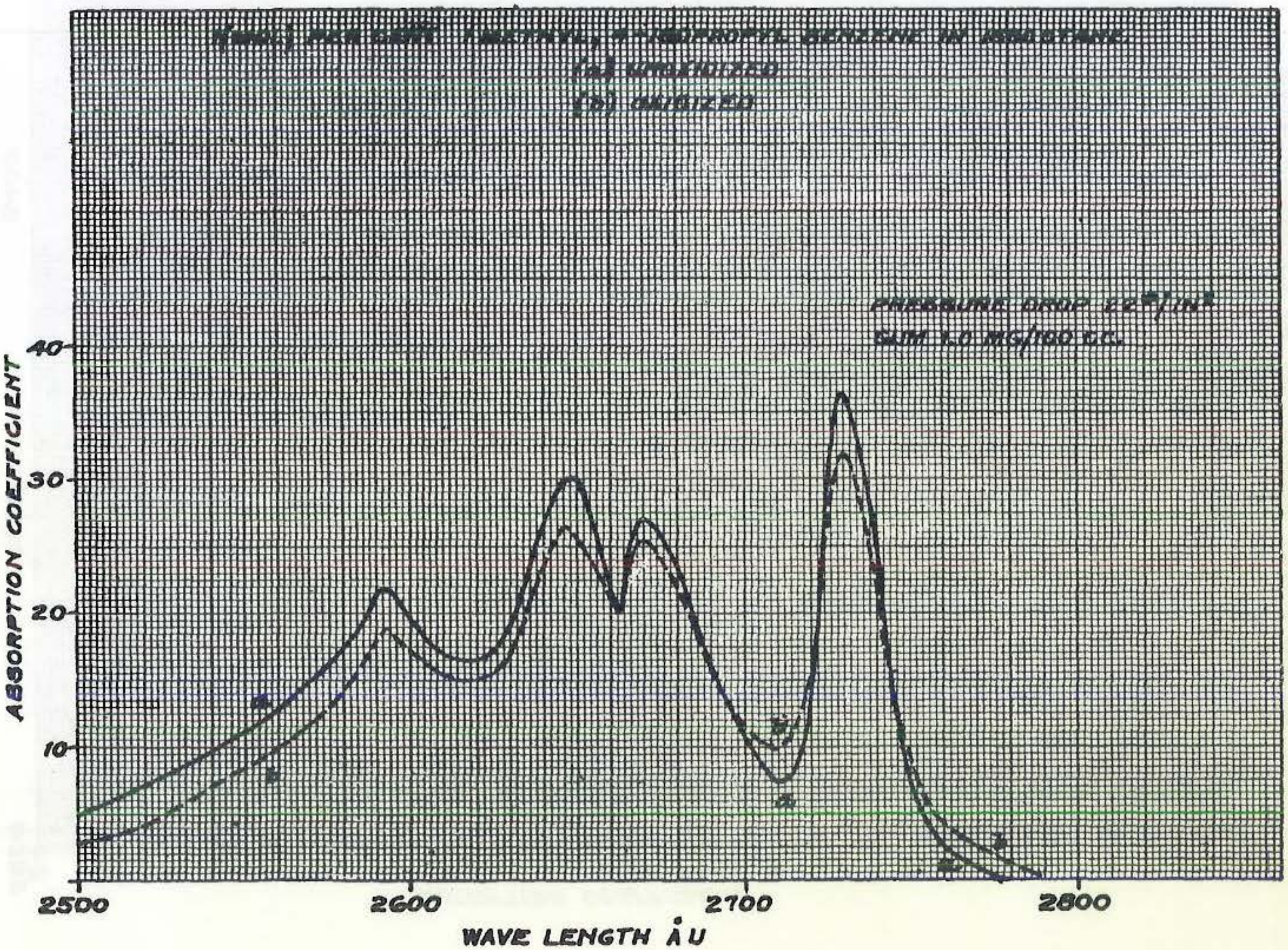
1(VOL.) PER CENT 1-METHYL, 4-ISOPROPYL BENZENE IN ISOOCTANE
(a) UNOXIDIZED
(b) OXIDIZED
PRESSURE DROP 22#/IN²
SUM 1.0 MG/100 CC.
ABSORPTION COEFFICIENT
10
20
30
40
a
b
2500
2600
2700
2800
WAVE LENGTH Å U

PLATE 9