[CONTRIBUTION FROM THE PURE OIL COMPANY]

AUTOXIDATION OF THE AMYLENES[1]

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A. Introduction

Although considerable work has already been done on the various phases of autoxidation, the field is of such magnitude that the special divisions of the subject suffer through lack of sufficient definite information concerning details.

One such division has to do with the autoxidation of the cracked gasolines. Much work still remains undone in this field. The chief reason for our lack of scientific knowledge in this especial field lies in the complex nature of the experimental material, namely, cracked gasoline. Such gasoline is doubtless a combination of paraffin, olefin, cyclic and aromatic hydrocarbons, along with hydrocarbons possessing in single molecules the characteristics of two or more of the classes mentioned.

In view of the situation as just presented, the authors of this paper felt that a study of the autoxidation of a comparatively simple series of olefins—the hydrocarbons with which autoxidation in gasolines appears most closely allied—might shed further light on the nature of the autoxidation phenomenon. Chief among the questions which such a study might answer is the one concerning the relation of autoxidation reactivity to the position of the double bond in the molecule, *i. e.*, to the nature and position of the groups attached to the unsaturated carbon atoms.

The simplest of such groups would be the butylenes, which number three. These compounds, however, are gaseous at ordinary temperatures, and in view of the fact that autoxidation in cracked gasolines appears to occur mainly in the liquid phase, it was thought unwise to use these materials in the present work.

The first group of olefins which are liquid at ordinary temperatures is that of the amylenes, five in number. These five are: (1) *n*-propylethylene, (2) isopropylethylene, (3) unsymmetrical methylethylethylene, (4) symmetrical methylethylethylene, (5) trimethylethylene.

The first systematic work on this group appears to have been done by Norris and Joubert.[2] These authors investigated the polymerizing action of sulfuric acid at various concentrations on the individual amylenes and found distinct differences in reactivity. Numbers 5 and 3 were classed as most reactive, Numbers 1 and 4 taking an intermediate position, while Number 2 was found to be comparatively unreactive.

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[1] Presented before the Petroleum Division of the American Chemical Society at Atlanta, Georgia, April 7–11, 1930.

[2] Norris and Joubert, THIS JOURNAL, 49, 873 (1927).

Work by Kirrmann,[3] however, cast doubt upon the reality of amylene No. 1 used by Norris and Joubert. In the present work, therefore, the authors have prepared amylene No. 1 by the interaction of allyl bromide on the Grignard reagent, ethylmagnesium bromide, using butyl ether as well as the amyl ethers as solvents and diluents. The reaction produced an amylene of boiling point 29–31°, in accord with the results of Kirrmann, as opposed to those of Norris and Joubert, who claimed a boiling point of 39–41°, for the product. It is likely that in the purification of their material, the last-named authors caused their amylene to undergo an intramolecular rearrangement of some type.

B. Experimental

In the present work amylenes 4 and 5 were made according to the methods given by Norris and Joubert. In the preparation of (5) heed was taken of the warning of Norris and Reuter[4] that in the dehydration of *tert.*-amyl alcohol a certain amount of amylene 3 is formed, and only the fraction boiling between 37.5 and 39° was used. Its D-line refractive index at 15° was 1.3898. The preparation of (4) appears to take place without any very great amount of side reaction. The fraction boiling between 35.5 and 37.5° was used in our experiments. The D-line refractive index at 15° for amylene No. 4 was 1.3840.

Amylenes 2 and 3 were made by the action of alcoholic potash on 1-iodo-3-methylbutane[5] and 1-iodo-2-methylbutane,[6] respectively, which had previously been prepared from their respective alcohols. Number 2 showed a boiling range of 21 to 24°, whereas No. 3 boiled almost constantly at 31.1°. Amylene No. 2 was further purified for Run No. 2 (see table) by treatment with 2:1 sulfuric acid at 0°. In this way a product of boiling range 20.5–21.5° was obtained. The D-line refractive index at 15° was 1.3682. The D-line refractive index for amylene No. 3 at 15° was 1.3800.

Amylene No. 1 was prepared as previously described. It was kept in contact with silver acetate in water over a period of weeks, with repeated distillations. Despite this, however, the product still showed a trace of bromine compound. Amylene No. 1 was finally freed from bromides by refluxing for four hours with metallic calcium and redistilling. It showed an almost constant boiling point of 30.0° (corr.). A refractive index determination at 21° gave a value of 1.3718 as compared with Kirrmann's value of 1.3714 for the same temperature. The refractive index reading (D-line) at 20° was 1.3731. An interesting side reaction in the production of amylene No. 1 was the formation of a hydrocarbon possessing a boiling point of around 20°. A fraction boiling between 20 and 24° was isolated.

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[3] Kirrmann, *Bull. soc. chim.*, **39**, 988 (1926).

[4] Norris and Reuter, This Journal, **49**, 2624 (1927).

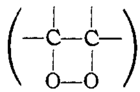
[5] Wischnegradsky, *Ann.*, **190**, 361 (1878).

[6] Le Bel, *Bull. soc. chim.*, [2] **25**, 546 (1876).

This fraction decolorized alkaline potassium permanganate very rapidly, and combined with bromine in the cold extremely energetically. While the exact nature of this compound is not known, it would appear probable that one is dealing in this instance with a substituted cyclopropane, probably ethylcyclopropane.

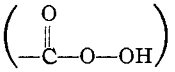
As to the method of determining the degree of oxidation, it was at first held expedient to use a manometric method, the lowering of the pressure in the reaction chambers being an indication of the amount of oxidation. During the course of the work, however, such erratic results were obtained that this method had to be abandoned. In its place was substituted a method based on the liberation of iodine by the bound (peroxide) oxygen.

According to the per-acid theory of autoxidation as suggested by us,[7] such oxidation proceeds in two steps: (1) the formation of a "moloxide"



$\left(\begin{array}{c} |\quad\;| \\ -\mathrm{C}-\mathrm{C}- \\ |\quad\;| \\ \mathrm{O}-\mathrm{O} \end{array}\right)$

from the breaking down of an oxidized per-ester; (2) the formation of a per-acid



$\left(\overset{\mathrm{O}}{\overset{\|}{-\mathrm{C}}}-\mathrm{O}-\mathrm{OH}\right)$

through the oxidation of aldehydes produced by the breaking of a moloxide molecule.

Such per-acids are known to react with double bonds quite energetically, and the per-acid theory postulates a per-ester as the initial reaction product. Unless this cycle is completed, the theory does not allow for progressive autoxidation.

There is considerable evidence to show that peroxides of the type R—O—O—R—to which class moloxides are structurally related—are incapable of liberating iodine from hydriodic acid and, in accordance with this view, not the moloxides but only the per-acids and per-esters would oxidize the hydriodic acid. For comparative purposes in this study, therefore, the authors feel that this method for evaluating the relative extent of autoxidation is permissible.

One cubic centimeter of the amylene to be tested was pipetted from a cold pipet into an iodine flask to which had been added 20 cc. of a 5% alcoholic potassium iodide solution. To this mixture was added 2 cc. of glacial acetic acid, and the flask allowed to stand in the dark for exactly three minutes. The contents of the flask were then rapidly titrated against a 0.01 *N* sodium thiosulfate solution. As is well known, the starch indicator in an alcoholic solution takes on an orange tinge rather than the usual violet. The end-point of the titration is nervertheless very sharp. The iodine color usually reappears shortly after the titration has been completed. This is to be disregarded, however, if one wishes (as in the present case) merely comparative results.

As reaction chambers were used common four-ounce oil bottles, each containing ten pieces of 6-mm. glass tubing, 15 cm. in length (to promote surface oxidation) and being fitted with a good cork stopper. Ten cc. of sample was placed in each bottle, the

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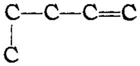
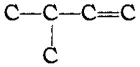
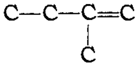
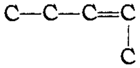
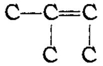
[7] Wagner and Hyman, Annual A. P. I. Meeting, December, 1929; *J. Inst. Pet. Tech.*, **15**, 676 (1929). Milas [*Proc. Nat. Acad. Sci.*, **14**, 844 (1928)] had previously shown perbenzoic acid to act as an autoxidation catalyst for olefinic substances.

oxygen being introduced by a glass tube reaching half-way to the bottom of the bottles. The oxygen was taken from a tank and allowed to run in to each bottle for ten seconds. Thereupon the bottle was corked immediately and the contents thoroughly agitated. Whenever the bottles were opened, they were placed in an ice-bath, in order to maintain approximately constant conditions and to prevent evaporation as much as possible.

As oxidation catalyst cobalt oleate was used. This compound was prepared by dissolving 1 part of c. p. hydrated cobaltous acetate in 10 parts of hot U. S. P. oleic acid, and passing a current of air through the mixture for two hours at a temperature between 125 and 150°. The resulting product is a deep brown liquid which turns deep red upon standing. It is completely soluble in the amylenes. To each 10 cc. of amylene was added two drops (0.0424 g.) of the catalyst. The oxidation was carried out in the dark, at a temperature of 15°.

Table I

Results of Experiments

		Run No. 1	Cc. of 0.01 *N* $Na_2S_2O_3$ used after			
	Compound	Type	11 hrs.	17 hrs.	35 hrs.	42 hrs.
1	*n*-Propylethylene	 $\mathrm{\underset{\underset{C}{\vert}}{C}{-}C{-}C{=}C}$	0.10	0.15	0.15	0.15
2	Isopropylethylene	 $\mathrm{C{-}\underset{\underset{C}{\vert}}{C}{-}C{=}C}$	.45	1.55	5.90	6.10
3	*Unsym.*-methylethylethylene	 $\mathrm{C{-}C{-}\underset{\underset{C}{\vert}}{C}{=}C}$	.10	0.10	0.10	0.10
4	*Sym.*-methylethylethylene	 $\mathrm{C{-}C{-}C{=}\underset{\underset{C}{\vert}}{C}}$	1.20	2.70	3.45	4.35
5	Trimethylethylene	 $\mathrm{C{-}\underset{\underset{C}{\vert}}{C}{=}\underset{\underset{C}{\vert}}{C}}$	2.65	5.30	5.20	9.85
6	Blank of No. 5	......	0.00	0.00	0.00	0.00

Run No. 2

	13 hrs.	19 hrs.	36 hrs.	84 hrs.	156 hrs.	252 hrs.
1	0.00	0.00	0.00	0.00	0.00	...
2	.00	.00	2.90	11.60	22.15	...
3	.00	.00	0.00	0.00	0.00	0.00
4	1.65	2.85	3.75	7.70	18.00	15.10
5	1.65	3.00	4.80	8.80	19.75	16.90
6	0.00	0.00	0.00	0.00	0.00	0.00

C. Conclusion

Of the two runs, the second is to be considered as more accurately expressing the reactivities of the amylenes toward autoxidation. The long induction period for amylene No. 2 may be explained by its vigorous purification just prior to use. On the other hand, the lack of an induction period in the autoxidation of amylenes Nos. 4 and 5 may be ascribed to minute quantities of peroxide which may have formed in these olefins during a short period of standing before use. An interesting point to note is the high reactivity of the amylene No. 2, once oxidation had begun, and the lesser but similar orders of reactivity of amylenes Nos. 4 and 5. The disappearance of peroxide at 252 hours is also of considerable interest.

Most noteworthy, however, is the fact that the results here recorded appear to bear little or no relationship to the results of the sulfuric acid polymerization experiments of Norris and Joubert.

A theory has been developed to explain the results herein recorded, and will be published at a later date. From the present data, however, it may be concluded that the *average* internal double bond is much more prone to autoxidation than is the *average* end double bond. It would, therefore, follow that in diolefins the internal double bond would be the first to be attacked. As a matter of record, the authors have previously reported[7] acrolein as being an important constituent among the products resulting from the autoxidation of cracked gasoline, an observation which is in accord with experiments reported herein.

The present paper is intended by the authors as a report of general work on autoxidation now in progress. It is hoped that further details will be ready for publication in the near future.

D. Summary

1. The autoxidation of the amylenes has been investigated.

2. Results indicate that, in general, internal double bonds are more readily oxidized by molecular oxygen than end double bonds.

3. Kirrmann's method of preparation of pentene-1 has been confirmed. A new hydrocarbon obtained as a by-product of this reaction is mentioned.

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[A Communication from the Laboratory of Organic Chemistry of the University of Wisconsin]

THE USE OF NICKEL AS A CATALYST FOR HYDROGENATION

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The hundreds of papers and patents published on the use of nickel as a catalyst for the hydrogenation of organic compounds might well be considered to render unnecessary any extended research in this field. In spite of this profusion of publications and in a sense because of it, a beginning has been made in what is intended to be a systematic investigation of the use of nickel as a catalyst for the hydrogenation and condensation of organic compounds especially with regard to selective reaction, *i. e.*, the modification of the proportion of simultaneous reactions through control of the temperature, pressure, reaction medium and character of the catalyst. For a number of reasons it does not seem that here or now is a suitable place or time for a comprehensive review of the extensive literature on the use of nickel as a catalyst. It must suffice for the present to refer to some of the