of rapic acid and of the greater part of the unsaturated acids remain in the solution in 90% alcohol, it is inferred that the acid isolated is undoubtedly erucic acid. A confirmatory test can be performed by reducing it to behenic acid with an active catalyst in a suitable solvent. This will be investigated later.

Tung Oil

The magnesium soaps from all oils examined (in the preceding paper) are either entirely or almost entirely soluble in 90% alcohol at the temperature of the *boiling* alcoholic soap solution. Tung oil is an exception, in that an abundance of white elastic magnesium soap may be prepared from it which is insoluble in 90% (by volume) alcohol even upon prolonged boiling under a reflux condenser. Since tung oil is said to contain mainly the glycerides of eleomargaric and oleic acids with small amounts of saturated acids, and since the magnesium soaps of oleic acid and small amounts of saturated acids are soluble in the boiling alcoholic solution, the insoluble substance is probably magnesium eleomargarate.

Technique of the Test.—The tung oil is saponified and the magnesium soaps are precipitated in the same manner as that described for rape oil. The mixture containing the insoluble magnesium soaps is filtered while almost boiling hot. The precipitate is washed with hot 90% alcohol and decomposed with dil. hydrochloric acid, preferably in the absence of air. The liberated acid has the strong odor characteristic of tung oil. The acid is soluble in cold, 90% alcohol and melts at about 44°. After 1 or 2 days' contact with the air, it absorbs oxygen and gradually changes to a dark brown, resinous mass. This change is greatly accelerated at elevated temperature. The yield of this acid (eleomargaric), obtained from the one sample of tung oil tested, was about 20%.

New York, N. Y.

THE MECHANISM OF THERMAL DECOMPOSITION OF THE PENTANES

By G. Calingaert

Received June 8, 1922

Normal and *iso*pentane, which constitute the lower-boiling fraction of petroleum ether, are at present of no technical use. The present writer has made a study of the product of their decomposition by heat, with a view to their possible utilization in other ways than as a fuel. If it were possible, by their partial decomposition, to obtain satisfactory yields of unsaturated hydrocarbons of 4 and 5 carbon atoms, then further treatment might produce acids, alcohols or other derivatives of higher commercial value than the original petroleum ether.

The pentanes, like organic compounds in general, are decomposed on being passed through a red-hot tube. The literature gives references to the products obtained in many cases. We find with hydrocarbons that the products of decomposition are generally the same, whatever hydrocarbon is tested. The percentage of hydrogen increases gradually, and the percentages of unsaturated hydrocarbon and methane increase up to 750°, but decrease beyond this temperature, which corresponds to the beginning of the formation of aromatic hydrocarbons.

It may be inferred from these facts that but a small amount of the decomposition products is obtained by means of the first reaction, and that the main yield may be considered as the final result of several successive reactions.

For these reasons, an investigation was made of the thermal decomposition of the pentanes, in the hope of determining the mechanism of the reaction, and limiting it to the first step of the decomposition.

Procedure

All of the experiments were conducted in such a way as to form products of the first decomposition of the pentanes and prevent, as far as possible, any further decomposition. To realize such conditions, I have, first, worked always at the lowest temperature at which the reaction proceeds at a reasonable rate; and second, maintained such a rate of flow of gas through the hot tube that but a small percentage of the pentane was decomposed.

In each case, a quantitative analysis of the decomposition products was made by the following methods. (1) In a known volume of the gas, the unsaturated hydrocarbons were determined by means of bromine water. (2) A gas-washing bottle filled with bromine and water was connected with the exit end of the furnace tube, in order to prepare a large amount of the bromides of the unsaturated hydrocarbons. These were then separated by fractional distillation, and identified by their boiling points or melting points and their percentages of bromine. (3) The saturated gases, after having passed through bromine, were fractionated and analyzed by explosion, using the method of P. Lebeau and A. Damiens.[1] On cooling these gases with liquid air, all but hydrogen is condensed. As, at this temperature, methane still has a vapor tension of a few millimeters, by using a mercury vacuum pump, a first fraction containing only hydrogen and methane can be separated. Further, by allowing the temperature to rise to certain definite points, one can by the same method extract, with the aid of the vacuum pump, mixtures containing but 2 of the gases present. In such mixtures the percentage of each of the components was determined by explosion with oxygen.

Combining the results obtained for the saturated gases with those given by the dibromides for the unsaturated part, we have prepared a complete table of the decomposition products.

Material

The material used was pentanes obtained by fractional distillation of petroleum ether. Their physical constants were: *n*-pentane, b. p. 35.7–

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[1] Lebeau and Damiens, *Ann. chim.*, [9] **8**, 221 (1921).

36.2°, d_{15} 0.6308; *iso*pentane, b. p. 27.6–28.2°, d_{15} 0.6245. The figures given by Sydney Young[2] are *n*-pentane, b. p. 36.0°, d_{15} 0.6307; *iso*pentane, b. p. 27.95°, d_{15} 0.6245.

Preliminary experiments showed that decomposition of the pentane became appreciable at about 600°, and this temperature was maintained within 3° during all further experiments. At this temperature, and with a rate of flow of $^1/_6$ gram mole per hour, only 30% of the original pentane was decomposed.

Experimental Results

Normal Pentane.—The first analysis with bromine water showed 44% of unsaturated hydrocarbons. The analysis of the saturated gas gave, for 100 volumes: hydrogen, 9%; methane, 21%; ethane, 45%; propane, 18%; pentane, 7%. The 7% of pentane is explained by the fact that, at the temperature at which the undecomposed pentane is separated from the gas produced (—20°), it has still an appreciable vapor tension, and consequently is not completely condensed.

After 3 fractionations, 35 g. of dibromides gave the following fractions.

Boiling point °C.	G.	Boiling point °C.	G.
<130	1.0	145–155	2.5
130–133	5.0	155–162	3.0
133–140	2.0	Residue	1.0
140–145	12.5	.....	...

The solid residue, crystallized twice from alcohol, gave colorless needles melting at 110°.

These results seem to show the presence of dibromo-ethane, b. p. 131°; dibromopropane, b. p. 142°; dibromobutane, b. p. 160°; and tetrabromobutane, m. p. 116°.

Recalculating these data on the basis of 44 moles of unsaturated and 56 moles of saturated hydrocarbons, we obtained,

H_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_2H_4	C_3H_6	C_4H_8	C_4H_6
5	12	26	10	0	12	10	24	3	6

These results correspond to a break of the molecule of normal pentane at the central atom of carbon, giving an ethyl and a propyl group, one of which is then saturated at the expense of the other, which becomes unsaturated, so as to give either ethane and propylene, (*a*) or ethylene and propane (*b*).

Considering only that hydrocarbon which is decomposed, 55% follows Reaction *a*, while 25% only is rearranged as shown in *b*. The largest part of the 20% remaining goes to form a methyl and a butyl group. In the latter case, it is always the lightest group which becomes saturated, giving methane and butylene.

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[2] Young, *J. Chem. Soc.*, **71**, 440 (1897).

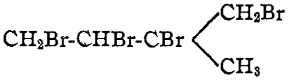
iso-**Pentane.**—The method of procedure was exactly as described in the case of *normal* pentane.

The first analysis with bromine water showed 40% of unsaturated hydrocarbons. The analysis of the saturated gases gave, for 100 volumes: hydrogen, 10%; methane, 50%; ethane, 38%; pentane, 2%.

After 4 fractionations 250 g. of the dibromides gave the following fractions:

B. p. ° C.	G.	% Br.	B. p. ° C.	G.	% Br
140–145	70	79.3	168–175	20	69.9
145–158	10	..	Residue	5	..
158–168	95	74.5	.....	..	..

The solid residue, after crystallization from alcohol, crystallized in colorless needles, m. p. 108°, and contained 84.1% of bromine. These data are compared below with the physical constants of pure compounds.

	B. p. ° C.	% Br		M. p. ° C.	% Br
CH_3-$CHBr$-CH_2Br	142	79.2	CH_2Br-$CHBr$-$CHBr$-CH_2Br	115	85.6
CH_2Br-$CHBr = (CH_3)_2$	149	74.0	 $CH_2Br\text{-}CHBr\text{-}CBr\begin{cases}CH_2Br\\CH_3\end{cases}$	116	82.5
CH_3-$CHBrCHBr$-CH_3	160	74.0			
CH_2Br-$CHBr$-CH_2-CH_3	166	74.0			
CH_2Br-$CHBr$-$CH =$ $(CH_3)_2$	173	69.2			

This demonstrates the presence of propylene, *n*-butylene, amylene, and small amounts of dienes of 4 and perhaps 5 carbon atoms.

Recalculating on the basis of 40% unsaturated and 60% saturated hydrocarbons, we obtain,

H_2	CH_4	C_2H_6	C_5H_{12}	C_3H_6	C_4H_8	C_5H_{10}	C_4H_6 C_5H_8
6	30	24	1	15	20	4	1

This shows that the molecule of *iso*pentane breaks on one or the other side of the tertiary carbon atom.

The first reaction gives a methane and an *iso*butane group which, always by saturation of the lighter group, give a methane group on the one hand and an ethyl- or dimethyl-ethylene (CH_2=CH—CH_2—CH_3 or CH_3—CH=CH—CH_3) on the other. Both of these seem to be present, for the boiling point of the corresponding dibromide fraction varies from 160° to 166°, the boiling points of the 2 dibromides.

A second reaction gives an ethyl and an *iso*propyl group. In this case, it is always the chain of two carbon atoms which becomes saturated, as neither ethylene nor propane is present.

Besides these two reactions, which utilize 90% of the pentane decomposed, a small amount of pentylene is formed, as shown by the last fraction of dibromide. We were unable to identify this pentylene, owing to our having only a few grams of its dibromide.

Finally, a part of the pentylene and butylene formed gave, by a secondary reaction, butadiene (erythrene) and pentadiene (isoprene).

In order to confirm this last hypothesis, a further cracking experiment was made on pure butylene. The resulting mixture contained 50% of unsaturated hydrocarbons. The saturated gas contained hydrogen and methane. The dibromides gave by fractionation the following values.

B. p. ° C.	G.	% Br		B. p. ° C.	G.	% Br
140–145	15	79.4		160–166	10	74.5
145–160	5	..		M. p.		
			Solid residue	110	1	84.6

These correspond to propylene, butadiene and undecomposed butylene. The results show that, at 600°, butylene itself is partly decomposed to give, besides a small amount of butadiene, a new break in the carbon chain.

Summary

1. It has been shown that *normal*- and *iso*pentane are decomposed at 600°, giving hydrogen and hydrocarbons, all containing 5 or fewer carbon atoms.

2. In both cases, the most important reaction, corresponding to about 90% of the decomposed pentane, consists in a break of the molecule at the central carbon, 1 of the 2 groups so formed being subsequently saturated at the expense of the other.

3. An interesting fact is the different behavior of the *n*-propyl *iso*propyl groups in presence of the same ethyl group. Both the *normal*- and the *iso*pentane can be cracked to form an ethyl and a propyl group, this latter being a *normal*-propyl group in the case of *normal*-pentane, and an *iso*propyl group in the case of *iso*pentane.

In the first case, however, whereas the *normal*-propyl group is able to give either a saturated or an unsaturated hydrocarbon, in the second case the *iso*propyl group, though in presence of the same ethyl group, is always transformed into propylene, as no propane is to be found in the products of the decomposition of *iso*pentane.

4. Only a small amount of pentane was broken between a primary and a secondary carbon atom, in the case of *normal*-pentane, and none in the *iso*pentane, which contains a tertiary carbon, where the tendency to break is much greater.

5. Secondary reactions involving the decomposition products gave saturated and unsaturated hydrocarbons containing fewer atoms of carbon. This explains the results of different experimenters who have found that, for the same hydrocarbon, on increasing the temperature of cracking, the percentage of hydrogen and methane increases.

6. Notwithstanding the ease of the reactions, and the rapid removal of the decomposition products, no satisfactory yields in unsaturated hydro-

carbons of 4 or 5 carbon atoms were obtained, a fact which seems to leave but little hope that the cracking of petroleum ether will provide an easy means for the preparation of synthetic organic compounds.

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[CONTRIBUTION FROM THE ORGANIC LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

THE ACTION OF HYDROGEN PEROXIDE UPON CERTAIN PHENYL-SUBSTITUTED URIC ACIDS

FOURTH PAPER ON PURINES

BY F. J. MOORE AND ELIZABETH S. GATEWOOD

Received July 10, 1922

In previous papers[1] it had been shown that the action of hydrogen peroxide upon uric acid may lead to two distinct series of products, according to experimental conditions. In a solution whose alkalinity is less than normal and whose temperature is above 80°, the products are allantoin and carbonyl di-urea, though the latter in a solution more alkaline than 0.5 N is transformed to cyanuric acid. At room temperature and in alkali more concentrated than normal, the product of oxidation is allantoxanic acid which, if the solution be acidified without removing the hydrogen peroxide, is oxidized in the acid solution to cyanuric acid.

These studies, however, revealed no intermediate between uric acid and the products mentioned, and threw no light upon any relationship which may exist between the mechanism of this reaction and that of the permanganate oxidation, which has been studied so intensively by Emil Fischer, Behrend and Biltz. Accordingly, after the publication of the third paper, Miss Ruth Thomas, working in this Laboratory, studied the action of hydrogen peroxide upon numerous purine derivatives including theobromine, caffeine, xanthine, guanine, 3-methyl-uric acid, 7-methyluric acid, 7-oxymethylene-uric acid, 9-methyl-uric acid and 3, 7-dimethyl-4,5-uric acid glycol.[2]

In summary it may be said that in all these cases the results were negative in the sense that they did not invite immediate further study. Some compounds were unaffected, some were decomposed by the alkali; in still other cases the reaction led to jelly-like mixtures. At some future time it may seem advisable to return to these reactions, but the immediate purpose of the experiments was to find substances which, when treated with hydrogen peroxide, would give homogeneous products in reasonable yields. The first compound which fulfilled these conditions was 9-phenyluric acid. From this compound Miss Thomas was able to obtain am-

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[1] Venable and Moore, THIS JOURNAL, **39**, 1750 (1917). Venable, *ibid.*, **40**, 1099 (1918). Moore and Thomas, *ibid.*, **40**, 1120 (1918).

[2] Miss Thomas, unpublished notes.