

CCXLIV.—*The Oxidation of n-Triacontane.*

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It is now known that Scotch paraffin wax fusing between 55° and 56°, and probably all similar waxes, are composed of ten to twelve *n*-hydrocarbons (J., 1926, 1420).

The oxidation of paraffin by air or oxygen has been described in this Journal, but in 1922 (J., 121, 501) it was shown that the synthetic hydrocarbons *n*-hexadecane and *n*-dotriacontane in the presence of 5% of turpentine suffered no change when treated with a current of air at 100° for 730 and 696 hours, respectively. Under similar conditions, paraffin wax reached a content of about 19% of oxygen. At that time, these observations led to the conclusion that the hydrocarbons present in the latter substance differed from those of the normal series.

Later it was found, however, that the presence of very small quantities of certain impurities in paraffin was capable of greatly prolonging the latent phase of the oxidation process, that characteristic period in this reaction when no change is observed.

Both of the above hydrocarbons had been synthesised from their halogen derivatives—octyl and cetyl iodide—purified by the ordinary method, and were judged from their constants and analyses to be pure. A sufficient amount of the specimen of hexadecane used in the work was available, and on being tested was found to contain traces of iodine, and there is but little doubt that the dotriacontane was contaminated in a similar manner. It was highly probable that these impurities had prolonged the latent period of the oxidation, and in order to test this view, a suitable hydrocarbon—*n*-triacontane—was synthesised by a method that did not involve the use of halogen derivatives.

Triacontane was prepared by the electrolysis of potassium palmitate (Peterson, *Z. Elektrochem.*, 1906, 12, 141). The palmitic acid used was Kahlbaum's purest preparation, and the resulting hydrocarbon (480 g.) was purified by crystallisation from benzene, followed by fractional distillation in a vacuum. It fused at 66.5°, and boiled at 304° (corr.)/15 mm.; the analysis is given in Table I.

During this preparation, about 70 g. of a hydrocarbon were isolated, liquid at the ordinary temperature, a description of which will be given in a later communication.

When triacontane and 5% of turpentine were treated at $95^{\circ} \pm 2^{\circ}$ with a current of air free from moisture and carbon dioxide, oxidation took place in a manner strikingly similar to that shown by paraffin wax or the hydrocarbons isolated from it. The analysis of the material after the passage of air for various periods is given in Table I, *a* being the duration of the air current in hours. The final product showed an acid value of 88.6.

TABLE I.
Oxidation of C₃₀H₆₂. t = 95° ± 2°.

<i>a.</i>		% C.	% H.	% O by diff.	<i>a.</i>	% C.	% H.	% O by diff.
	Hydrocarbon	84.9	14.9	—	506	80.5	13.6	5.9
173		82.5	14.5	3.0	577	79.1	13.0	7.9
266		82.4	14.5	3.1	748	78.0	12.8	9.2
341		82.3	14.3	3.4	865	76.1	12.6	11.3
413		81.3	14.0	4.7	1009	75.7	12.2	12.1

If the data in Table I be compared with those for paraffin wax at 100° (J., 1924, 125, 387), it will be seen that in both cases there is a halt in the progress of the oxidation when the oxidised material contains about 3% of oxygen, and a similar but less well-marked phenomenon when the content has reached 8% of this element.

With the above hydrocarbon at the temperature mentioned, an oxygen content of 7% is reached in 550 hours; at 100° , paraffin wax requires 790 hours, the hydrocarbon C₂₂H₄₆ isolated from paraffin 460 hours, and C₂₉H₆₀ from the same source 420 hours (compare J., 1924, 125, 383).

Products of the Oxidation.—(1) During the oxidation of paraffin wax, of the hydrocarbons isolated from it, and of triacontane itself, carbon dioxide and formic acid are formed. The amounts of these were determined by passing the gases through an excess of barium hydroxide solution. Triacontane gave 4.3 g. of carbon dioxide per 100 g. of hydrocarbon oxidised, and in the other cases the amount varied between 4.6 and 6.3 g. The amount of carbon in the form of formic acid produced from triacontane was 0.6 g. per 100 g. oxidised, and in the other cases varied between 1.0 and 1.3 g.

(2) The products of the oxidation were freed from unoxidised triacontane by several crystallisations from fifteen times the volume of acetone. The unchanged hydrocarbon, insoluble in this solvent, amounted to 21%. In the case of paraffin wax under comparable conditions, the corresponding amount lies between 25 and 30%.

(3) The oxidised triacontane, consisting of acids and inert material, was then saponified with an alcoholic solution of caustic potash, water added until 50% was present, and the inert products were extracted with large quantities of light petroleum. The acids amounted to 64%, whereas in the case of paraffin wax they lay between 58 and 69% in different experiments.

Acidic Products of the Oxidation.—(1) The acids were steam-distilled, but the amount of oily distillate was too small for identification. The water in the distilling flask, however, had dissolved a small quantity of a substance which consisted chiefly of succinic acid, although the amount isolated was insufficient for complete purification. It fused at 176°, and at 178–179° when mixed with succinic acid (m. p. 181°), and its molecular weight by titration was 119 (Found: C, 41.2; H, 4.3. Calc. for $C_4H_6O_4$: C, 40.7; H, 5.1%; *M*, 118).

(2) The cake of dry acids from the previous operation was recrystallised several times from chloroform followed by acetone, and about 9% of a mixture of white, crystalline acids was obtained. After long-continued fractional crystallisation, these were found to consist chiefly of $C_{26}H_{52}O_2$, which appeared to be identical with cerotic acid, and a small quantity of $C_{24}H_{48}O_2$. Both these acids had been previously isolated in this laboratory from products of the oxidation of paraffin wax.

The specimen of cerotic acid used for the comparison was prepared for us by the Eastman Kodak Co. It had been isolated from beeswax and purified by the fractionation of its methyl ester. Both this acid and the corresponding one mentioned above were further purified by conversion, in methyl-alcoholic solution, into the barium salt, which was extracted with ether and finally with acetone. The acids recovered from these salts by solution in hot acetic acid were repeatedly crystallised from acetone and finally from light petroleum. The full comparison is given in Table II.

The data given for the corresponding acids from paraffin wax (*a*) and (*b*) were for specimens isolated by different observers and their preparation will be described in another communication. We have to thank Mr. Piper, who is undertaking an investigation of these other acids, for the X-ray data. He informs us that, as regards the high values in the above table, the error is about 1%. We point out that the melting points of the above acids are about 10° lower than that of the synthetic acid of the same carbon content, which, according to Levene and Taylor, fuses at 88.5° (*J. Biol. Chem.*, 1924, 59, 919). We leave to a later date the discussion of this acid and that melting at 74°, of acid value 152, which is probably $C_{24}H_{48}O_2$, together with a series of what are believed to be

TABLE II.

Source.	Beeswax.		Paraffin wax.	
	$C_{30}H_{62}$.	$C_{30}H_{62}$.	(a).	(b).
M. p.	77.5°	78°	80°	76°
Mixed m. p.	77.5—78°			
Acid value. (Calc. for $C_{26}H_{52}O_2$, 141)	144	145	141	146
Calc. for { C 78.8%	78.6%	78.4%	79.1%	78.9%
$C_{26}H_{52}O_2$ { H 13.1%	13.1%	13.2%	13.3%	13.1%
X-Ray spacing, "pressed." Å.	68.03	68.85	68.8	68.4
M. p. of methyl ester. (Previous observers, 60—62°)	60.5°	63.5°	62—3°	62°
Mixed m. p.	62°			
M. p. of ethyl ester. (Previous observers, 59—60°)	58°	60.5°		
Mixed m. p.	59°			
X-Ray spacing, "pressed." Å. Ethyl ester.	39.15	39.0		

analogous acids, which have been isolated from the oxidation products of paraffin wax.

(3) The main bulk of the acids, from which cerotic acid and the acid $C_{24}H_{48}O_2$ have been removed, is a complex mixture of monobasic and oxy-acids which cannot be separated from the small amount of inert material present by conversion into barium salts and extraction with solvents. The mixture is as difficult to deal with as that of the corresponding material from paraffin wax.

The material was converted into methyl esters, of which about 38% could be distilled without decomposition in a vacuum of 3 mm., this amount corresponding closely with that observed in the case of the similar complex obtained from paraffin wax. The distillate boiled between 140° and 205°/6 mm. and on standing in the ice-chest deposited a crystalline substance. The acids obtained from this were fractionally crystallised from acetone and finally two were isolated in small quantities: (A) M. p. 63°, acid value 188. Found: C, 76.1, 76.3; H, 12.7, 12.7%. The pressed X-ray spacings were Å. 52.11. Provisionally this is regarded as $C_{20}H_{40}O_2$ (Calc.: Acid value, 179; C, 76.9; H, 12.8%). (B) M. p. 53.4°. Found: C, 74.8, 75.0; H, 12.5, 12.4%. The pressed X-ray spacings = Å. 46.56. This is provisionally regarded as $C_{16}H_{32}O_2$ (Calc.: C, 75.0; H, 12.5%), but is probably contaminated with an acid of higher carbon content.

(4) The residue of esters which could not be distilled gave a

small quantity of an acid, fusing at 68° after repeated crystallisation from glacial acetic acid (Found: C, 76.9; H, 12.6%). It is probably an impure specimen of $C_{22}H_{44}O_2$ (Calc.: C, 77.6; H, 12.9%).

Acids similar to those just described have been isolated in larger quantities from the products of the oxidation of paraffin wax.

Inert Products of the Oxidation.—Following the method previously described (J., 1926, 2377), the non-acidic products of the oxidation were repeatedly crystallised from five times their weight of acetone, and thus separated into a relatively insoluble, white, crystalline mass, comprised chiefly of ketones and dioxy-products constituting together about 46% of the mixture, and a more soluble coloured mixture of more highly oxidised hydrocarbon, which was not further examined.

(i) The crystalline mixture fused at 58—59°. It was acetylated and the more soluble acetyl derivatives were separated by their greater solubility in acetone. The acetates were decomposed, and the resulting alcohol after purification fused at 69° (Found: C, 79.4; H, 13.5. Calc. for $C_{30}H_{60}O_2$: C, 79.6; H, 13.2%). It was either a ketonic alcohol or a dihydroxy-derivative, but the amount obtained was insufficient for further examination. The residual material, from which a certain part of the dioxy-substance had been separated, fused at 60—61° and contained C, 80.7; H, 14.2%. It was chiefly composed of ketones and dioxy-derivatives.

(ii) This mixture was treated with hydroxylamine, and the resulting oxime separated by its greater solubility in alcohol from the other substances present. The oxime itself could not be purified, but on saponification it gave a well-defined, crystalline ketone, m. p. 62.5° (Found: C, 82.0; H, 13.8. Calc. for $C_{30}H_{60}O$: C, 82.5; H, 13.7%).

Mr. Piper examined this specimen by X-rays and informed us that it contained 30 carbon atoms and, judging from the intensity distribution, the oxygen was situated most probably on the fourth carbon atom. (See J., 1926, 2381, for corresponding ketones with lower carbon content obtained from paraffin wax.)

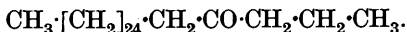
Summary.

We have shown the striking similarity between the oxidation of synthetic triacontane, the mixture of solid *n*-hydrocarbons termed paraffin wax, and the pure constituents isolated from the latter. This similarity extends, not only to the velocity of oxidation, but to the nature and amounts of the products formed.

The highest acid present among the acidic products of the oxidation of triacontane has a carbon content of 26 atoms and appears to be identical with cerotic acid obtained from beeswax. This

acid fuses 10° lower than the corresponding synthetic acid, a phenomenon noticed with other acids obtained from paraffin wax, which will be discussed at a later date.

Support has been obtained for the view expressed previously (J., 1926, 2383) that in the oxidation of hydrocarbons such as triacontane the first product is a secondary alcohol, which then passes to a ketone. The latter has been isolated and found to have a carbon content of 30 atoms. X-Ray analysis indicates that the oxygen is situated on the fourth carbon atom; on further oxidation, the chain breaks, and the fact that a C_{26} acid results leads to the conclusion that the ketone has the structure



This view is also supported by the presence of succinic acid among the products of the reaction.

The amount of acids with high carbon content resulting from the oxidation of such long-chain hydrocarbons is always very small. Probably, simultaneously with the formation of the secondary alcohol followed by that of the ketone and their breakdown into acids, there occurs the further oxidation of the mono-oxy-derivative first formed to polyhydroxy-derivatives, which on further oxidation pass to ketones and then break down to acids and oxy-acids of still smaller carbon content.

Our thanks are due to the Colston Research Society for grants towards the expenses of this work.

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[Received, June 1st, 1927.]