

CCCXVI.—*The Non-acidic Oxidation Products of Paraffin Wax.*

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THE majority of those who have investigated the products resulting from the oxidation of paraffin by air or oxygen have been concerned with the acidic materials which are formed, and, as regards the non-acidic substances, have stated their amount, speculated as to their nature, and shown that they decreased as the temperature of the oxidation was increased, or as the period of that process was prolonged.

Grun, however, in 1920 (*Ber.*, **53**, 987) attempted to elucidate their nature, and although he did not succeed in isolating in a pure state any of the classes of substances present, nor publish any analyses of his products, yet he showed the presence of alcohols and carbonyl derivatives. The carbonyl compounds were identified as a class, and the approximate amount present was estimated, by the determination of the acetyl value of a mixture containing alcohols before and after reduction. Grun claimed to have obtained stearic acid by the oxidation of a fraction of these carbonyl derivatives, but did not publish any of the constants or analytical values obtained for his product. Even if this acid was isolated, no light is thrown on the nature of its source, since it could have been produced equally well by the simple oxidation of an aldehyde, or by the disruptive oxidation of a ketone.

We have again investigated these non-acidic materials and have succeeded in extending Grun's observations and shown that they consist of secondary alcohols and ketones and their further oxidation products. The work, however, has proved difficult, since we have been unable to find any derivatives of these substances which were capable of purification by crystallisation.

It is certain that this mixture contains the primary oxidation products of paraffin, and since Piper (*J.*, 1925, **127**, 2194) has shown that the hydrocarbons isolated by one of us from paraffin wax are *n*-hydrocarbons, it becomes of importance to determine the nature of the alcohols and carbonyl derivatives present, in order to obtain some knowledge of the points at which air or oxygen first attacks the long carbon chains.

1. *Separation of the Oxidation Products.*—The paraffin used in the investigations which are being carried out in these laboratories is of Scotch origin and melts at 55–56°. As previously described (*J.*, 1922, **121**, 496), it was oxidised at 100° in the presence of 5% of turpentine by a rapid current of dry air over a period of 1200

hours. The resulting material was crystallised from fifteen times its weight of acetone. The oxidation products were relatively soluble, and the main bulk of unchanged paraffin crystallised on cooling. If this process was repeated with these hydrocarbons, they were obtained free from oxidised material, although the soluble oxidised product always contained small amounts of unchanged hydrocarbons. In different experiments the unoxidised hydrocarbons amounted to between 25 and 30% of the crude product from the oxidation; they are capable of further oxidation by the above method.

Approximately one-fifth of the oxidised material recovered from the acetone was composed of anhydrides, and esters constituted a larger proportion of the mixture than the free alcohols. This mixture was saponified in alcoholic solution with excess of caustic potash in order to decompose these substances, and the resulting solution was diluted with water until the whole contained 50%. On repeatedly shaking this solution with large volumes of light petroleum, more than 90% of the non-acidic products were extracted. In different experiments these substances varied between 28 and 39%, and the acidic products, obtained from the solution of their alkaline salts, from 69 to 58%.

2. *Partial Separation of Mono- and Di-oxy-compounds.*—The mixture of alcohols and carbonyl compounds, together with dioxy-derivatives and some unoxidised hydrocarbons—constituting, after saponification, the non-acidic products of the oxidation—may be partly separated into mono- and di-oxy-substances by repeated crystallisation from eight times its weight of acetone.

In different experiments, the white, crystalline mixture of mono-oxy-compounds and hydrocarbons, with small quantities of dioxy-derivatives of the higher hydrocarbons, varied from 62 to 66% of the total non-acidic material.

The dioxy-, with small quantities of polyoxy-, and mono-oxy-derivatives of low molecular weight, constituted between 38 and 34% of the mixture. It formed a brown, non-crystalline, soft wax, very soluble in all organic solvents, and decomposed on distillation in a vacuum.

3. *Treatment of the Mixture of Mono-oxy-substances.*—On fractionating the mono-oxy-mixture in a vacuum of 0.3 mm. it was not found possible to effect a separation of alcohols, ketones and hydrocarbons, although by far the greater part of the dioxy-substances of higher boiling point, which could not be distilled without decomposition, was found in the residue.

The various fractions were then acetylated with acetic anhydride; the products were liquids which deposited a certain quantity of

ketones and hydrocarbons on cooling. The greater part of these impurities crystallised when an acetone solution of the mixture was kept in the ice chamber for some days. The separation of ketones and hydrocarbons is described in section 5.

After the above treatment the lowest-boiling fraction was saponified, and the resulting alcohol converted into the phthalic acid ester. This substance was purified by means of its barium salt, of which two different preparations gave, by titration, *M* (for the alcohol) 337, 328 (Found for the acetate: C, 77.6; H, 13.1. The alcohol $C_{22}H_{46}O$ requires *M*, 326. Its acetate, $C_{24}H_{48}O_2$, requires C, 78.2; H, 13.1%). This indicated clearly the presence of an alcohol of the same carbon content as the lowest hydrocarbon, $C_{22}H_{46}$, known to be present in the paraffin wax used in this work.

The purified acetates obtained from the remaining fractions were again fractionated in a vacuum of 0.1 mm. They boiled between 184° and 220°. In order to determine the alcohols of minimum carbon content the lowest fraction was analysed, and since the highest was contaminated with dioxy-material, an intermediate one was investigated. The results obtained were as follows:

(1) Acetate fraction, b. p. 184—189°. Found: C, 78.6; H, 13.3; sap. value, 140. $C_{26}H_{52}O_2$ requires C, 78.8; H, 13.1%; sap. value, 141. The alcohol obtained from this acetate, on recrystallisation from acetone, melted at 51.5° (Found: C, 80.6; H, 14.4; *M*, ebullioscopic in chloroform, 343. $C_{24}H_{50}O$ requires C, 81.3; H, 14.1%; *M*, 354).

(2) Acetate fraction, b. p. 204—212°. Found: C, 78.2; H, 13.1; sap. value, 135. Mol. refractivity, 128.3. $C_{27}H_{54}O_2$ requires C, 78.9; H, 13.2%; sap. value, 136.8; mol. refractivity, 128.4. The alcohol obtained from this acetate fused at 61.6° (Found: C, 81.4; H, 14.1; *M*, in chloroform, 369. $C_{25}H_{52}O$ requires C, 81.4; H, 14.2%; *M*, 368).

Our thanks are due to Mr. N. E. Wood for repeating the above separation with another and larger specimen of acetates which was purified as described above. After the mixture had been fractionated and each fraction again purified, the resulting esters, which melted in the case of the lowest indefinitely at 0° and the highest at 9°, were converted into alcohols and repeatedly recrystallised from acetone followed by benzene until substances of constant melting point were obtained. Three alcohols were isolated in quantity; the most fusible one melted at 59° (Found: C, 81.6; H, 14.2%), another fused at 63.4° (Found: C, 81.0; H, 14.3%), and the least soluble melted at 66.5° (Found: C, 82.0; H, 14.4%). These alcohols are snow-white, microcrystalline powders, and the

crystals appear to belong to the hexagonal systems. An X-ray examination of these specimens will be published later.

Although there is but little doubt that these substances are not pure, yet the analyses again point very clearly to the presence of alcohols of similar carbon content to two of the hydrocarbons present in paraffin, *viz.*, $C_{24}H_{50}$ and $C_{25}H_{52}$. A very prolonged fractionation, probably similar to that required in the case of the hydrocarbons themselves, would be necessary before pure alcohols could be isolated.

In the fractionation of these acetates there was always a high-boiling residue which on analysis was shown to contain dioxy-substances.

4. *Nature of the Alcohols.*—The fractionation of the purified acetates had given a series of what we expected would prove to be primary alcohols (two only have been described above), and it was hoped that it would have been possible to examine these more fully in the form of their corresponding acids. They gave, however, no acids or evolution of hydrogen when heated with potash and potash lime (Hell reaction, *Annalen*, 1884, 223, 269), and it was clear that the hydroxy-derivatives formed in the oxidation were secondary alcohols, since paraffin contains only *n*-hydrocarbons. The small yields and the difficulty with which phthalic acid esters were formed from the alcohols supported this conclusion.

The action of a series of oxidising agents on these alcohols was investigated, but the results did not warrant further work. If the acids resulted, they were obtained in small yield and of lower molecular magnitude than the alcohols used, or were gummy transparent materials difficult to investigate. One of the products of oxidation with potassium permanganate in acetic acid solution was isolated; it appeared to be identical with the dioxy-substance previously mentioned (Found: C, 79.3; H, 13.5%. The average analysis of the dioxy-material is C, 79.3; H, 13.7%).

5. *Separation of the Carbonyl Compounds.*—The method used in the isolation of the mixture of carbonyl compounds and hydrocarbons from the alcohols has been previously mentioned (section 3). These derivatives were obtained from the various fractions of alcohol-acetates, but those of higher boiling point could not be completely freed from acetates by the method described.

Three fractions were selected and boiled in alcoholic solution with hydroxylamine. The resulting oximes were separated from the hydrocarbons by taking advantage of their greater solubility in acetone, and purified by treatment with cold alcohol, in which they were readily soluble. The oximes were viscous oils and gave white, well-defined, crystalline ketones on hydrolysis. These

ketones showed no acetyl value and hence were free from alcohols, but we were unable to separate the diketones with which they were contaminated.

Three specimens of ketones prepared in this manner from different fractions were purified by crystallisation from acetone and gave the data mentioned below. In the first two cases, the ketones were reduced with sodium in amyl alcohol to the corresponding alcohols, for which analytical data are also given, and these alcohols were further converted into their liquid acetates, which were analysed. The data obtained were interpreted in conjunction with the results of X-ray analysis, a summary of which is given below.

1. *Ketone*, m. p. 51.5–53°. Found: C, 80.8; H, 13.9. $C_{26}H_{52}O$ requires C, 82.0; H, 13.8%.

Secondary alcohol, m. p. 51–52°. Found: C, 80.3; H, 14.1; acetyl value, 123; *M*, ebullioscopic in chloroform, 374. $C_{26}H_{54}O$ requires C, 81.6; H, 14.2%; acetyl value, 132; *M*, 382.

The acetate of the secondary alcohol. Found: C, 78.4; H, 13.6. $C_{28}H_{56}O_2$ requires C, 79.2; H, 13.3%.

2. *Ketone*, m. p. 57–58°. Found: C, 80.9; H, 13.8. $C_{28}H_{56}O$ requires C, 82.3; H, 13.8%.

Secondary alcohol, m. p. 59–60°. Found: C, 80.3; H, 14.1; acetyl value, 125; *M*, ebullioscopic in chloroform, 391. $C_{28}H_{58}O$ requires C, 81.8; H, 14.2%; acetyl value, 124; *M*, 410.

The acetate of the secondary alcohol. Found: C, 78.8; H, 13.4. $C_{30}H_{60}O_2$ requires C, 79.6; H, 13.4%.

3. *Ketone*, m. p. 58.5–59.6°. Found: C, 81.2; H, 13.6. $C_{29}H_{58}O$ requires C, 82.4; H, 13.8%.

The above data show that none of these ketones was pure and it is probable that they were all contaminated with diketones. When the alcohols mentioned above were heated with potash and potash lime, they were not converted into acids, and gave no evolution of hydrogen. There can be no doubt, therefore, that they were secondary alcohols, and that the carbonyl derivatives from which they were obtained were ketones. This view was supported by an X-ray examination of these derivatives for which our best thanks are due to Mr. S. H. Piper. The results of this analysis, which will be published in a later communication, showed that specimen 1 had certainly a carbon-chain length of 26 atoms with the ketonic oxygen atom three (or four) from the end, specimen 2 probably a chain of 28 carbons, and specimen 3 a chain of 29 atoms, in both cases the oxygen atom being probably situated on the third (or fourth) carbon atom. These ketones have the same carbon content as three *n*-hydrocarbons known to be present in the paraffin wax used in this investigation, *viz.*, $C_{26}H_{54}$, $C_{28}H_{58}$, $C_{29}H_{60}$.

6. *Dioxy-derivatives*.—The method used for the separation of the soluble mixture of dioxy-materials has been described in section 2. This mixture gave on analysis C, 79.8; H, 13.3%, and an acetyl value of approximately 100.

After acetylation and treatment of the resulting product with cold alcohol, about 7% of monoketones crystallised, and the residual brown oil gave on analysis C, 76.6; H, 12.6%; acetyl value, 100; *M*, 407 in chloroform, 413 in benzene. These data approximate to those required for an acetate $C_{26}H_{50}O_3$, viz., C, 76.0; H, 12.3%; acetyl value, 137; *M*, 410. The low acetyl value, however, indicates that the main constituent of the mixture is a hydroxy-carbonyl derivative of about the same average carbon content as the paraffins which had been oxidised. No acidic material could be obtained from this substance by heating with potash lime at 300°.

We were unable to devise any satisfactory method for the separation of this mixture, although a partial one was effected by shaking it with five times its weight of cold methyl alcohol, and an examination was made of that fraction (55% of the total material) which was soluble in that solvent at 0°. These acetates formed an orange-coloured oil, of saponification value 143. On saponification, they gave waxes very soluble in all organic solvents. The acetates were fractionated four times in a vacuum of 1 mm.; the main bulk boiled between 190° and 270° and of the fractions obtained, three were investigated: (A) b. p. 190—200°, (B) 220—230°, (C) 230—245°. The residue contained tri- or poly-oxy-derivatives and was not further examined.

The lowest fraction (A) consisted largely of monooxy-substance. The alcohols obtained from it gave, by the phthalic acid ester method, an impure alcohol, $C_{22}H_{46}O$ (*M*, 326), the molecular weight of which in chloroform was 311 and in benzene 323. Its acetyl value was 173, whereas that calculated for the above alcohol is 152, an indication that the impurity present was a dihydroxy-alcohol.

The second fraction (B) gave on analysis C, 75.4; H, 12.1%; saponification value, 150. $C_{24}H_{46}O_3$ requires C, 75.3; H, 12.1%; saponification value, 146.7. In spite of the correspondence of these data, however, there was no doubt that the substance was a mixture. The saponified products from this material when treated by the phthalic acid ester method, gave an impure *ketonic alcohol* which on analysis gave C, 76.9; H, 13.1%; *M*, 347 in chloroform and 352 in benzene. $C_{24}H_{48}O_2$ requires C, 78.2; H, 13.1%; *M*, 368. The acetate obtained from this derivative gave C, 74.0; H, 12.1%; saponification value, 189. The acetate of a ketonic alcohol, $C_{26}H_{50}O_3$, requires C, 76.0; H, 12.3%; saponification value, 136.8.

The impurity present was probably dihydric alcohols. The third fraction (C) gave on analysis C, 75.3; H, 12.0%; saponification value, 155. On reduction with sodium in amyl alcohol the acetyl value of the resulting product was 215, again pointing to the presence of hydroxy-carbonyl derivatives.

We concluded that the mixture of dioxy-material was composed of hydroxy-ketones and dihydroxy-alcohols and diketones. It was clear that the large amount of time required to effect the complete separation of such a mixture, or indeed that of the mono-alcohols and ketones, would scarcely be commensurate with the results that might be obtained. If crystalline derivatives, however, of the various groups described could be prepared, then the methods we have outlined, coupled with the fractional crystallisation of such derivatives, would finally enable pure materials to be isolated from the various mixtures mentioned in this communication, with relative ease in the case of alcohols and ketones but with much greater difficulty in the others.

Since we now know that the paraffin wax under investigation, and probably all such paraffins, are composed of a mixture of *n*-hydrocarbons, it is proposed to study the oxidation products of one of the suitable synthetic *n*-hydrocarbons under the same conditions that we have employed in the case of paraffin; such an investigation should not present the great difficulties we have met with.

Summary.

The investigation of the very complex mixture of non-acidic substances found among the products of the air-oxidation of paraffin wax at 100° has shown the great difficulty involved in isolating pure materials.

The preliminary survey published by Grun, however, has been considerably extended and it has been established that secondary alcohols and ketones are present, and with less certainty dihydroxy-alcohols, hydroxy-ketones, and diketones. Primary alcohols, if formed at all, which appears unlikely, must pass immediately to acids, since they are not present in the partly oxidised wax.

These non-acidic products diminish in amount as the oxidation proceeds and are replaced by acids. It has been shown that the various secondary alcohols and ketones which were isolated have, in all probability, the same carbon content as six out of the seven normal hydrocarbons comprising the greater part of paraffin wax.

The ketones are derived from the secondary alcohols which are the primary products of the oxidation, and the point at which the carbon chain is attacked by oxygen was shown, by an *X*-ray examination of these ketones, to be the third (or fourth) atom from the end.

On further oxidation the ketones may break down to acids of smaller carbon content. In a later communication it will be shown that the highest acid formed in the oxidation has a carbon content of 28 atoms, whereas the highest hydrocarbon present in any quantity in paraffin is $C_{31}H_{64}$.

It is also possible that alcohols and ketones may be oxidised to dihydric alcohols, hydroxy-ketones, and diketones before the final stage of acids is reached.

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