270. *Radical Isomerisation during the Gaseous Oxidation of 2,3-Dimethylbutane.*

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Studies of the slow oxidation of 2,3-dimethylbutane show the presence of pinacolone and pinacolyl alcohol among the products. The formation of these compounds must involve isomerisation of intermediate free radicals and it is shown that this is more likely to occur in oxygenated radicals than at the alkyl radical stage. Possible reasons are discussed for the absence of these compounds among the oxidation products of 2,2-dimethylbutane.

THE development of gas chromatography has greatly facilitated analysis of the combustion products of hydrocarbons [1] and their simple derivatives [2] and, in particular, individual isomers and homologues may now be readily identified and estimated. It is sometimes difficult to account for the formation of certain of these products unless isomerisation, often involving migration of an alkyl group, is assumed to occur in one or more of the precursors. Alkylperoxy-radicals, which are believed to survive many collisions before reaction,[3] have been supposed to undergo intramolecular rearrangement in several combustion systems,[4,5] and direct support for this has recently been obtained from isotopic tracer studies.[6,7]

This paper provides evidence for the isomerisation of free radicals formed during the gaseous oxidation of 2,3-dimethylbutane. Previous work [8] suggests that attack on this compound takes place principally at the tertiary CH groups and it is shown here that certain of the intermediate products can only be accounted for in terms of intramolecular rearrangement of species resulting from initial oxidation at these positions.

EXPERIMENTAL

Materials.—2,3-Dimethylbutane used in preliminary work was found to contain 1—2% of the isomeric 2,2-dimethylbutane (neohexane). Since the latter compound was at first suspected to be the source of the small amounts of pinacolone and pinacolyl alcohol detected, very pure samples of both isomers were later kindly supplied by the British Petroleum Company and these were subsequently used for all quantitative measurements.

Apparatus.—A conventional static vacuum-system was used for the controlled oxidation of the two hexanes. Mixtures of hydrocarbon vapour and oxygen were introduced at known pressures into a heated cylindrical Pyrex vessel (150 ml.), and the progress of the reaction was followed manometrically and by periodic analysis.

Analytical Procedure.—The contents of the reaction vessel were withdrawn at various stages of oxidation and were first separated into condensable and non-condensable fractions by passage through traps at −178°. Both fractions were then analysed by gas chromatography, the identity of the products being checked by artificial addition of each of the components thought to be present. For the analysis of condensable products, partition columns containing two different stationary phases were used, polyethylene glycol (*M*, 400) for oxygenated compounds

[1] Yokley and Ferguson, *Combustion and Flame*, 1958, **2**, 117; Kyryacos, Menapace, and Boord, *Analyt. Chem.*, 1959, **31**, 222; Sandler and Beech, *Canad. J Chem.*, 1960, **38**, 1455; Cullis, Fish, Hardy, and Warwicker, *Chem. and Ind.*, 1961, p. 1158.

[2] Cullis and Warwicker, *Proc. Roy. Soc.*, 1961, *A*, **264**, 392.

[3] McDowell, *Discuss. Faraday Soc.*, 1951, **10**, 322; Small and Ubbelohde, *J. Appl. Chem.*, 1953, **3**, 193.

[4] Barusch, Neu, Payne, and Thomas, *Ind. Eng. Chem.*, 1951, **43**, 2766; Fok and Nalbandyan, *Doklady Akad. Nauk S.S.S.R.*, 1952, **86**, 589; 1953, **89**, 725; Rust and Collamer, *J. Amer. Chem. Soc.*, 1954, **76**, 1055; Cullis and Waddington, *Proc. Roy. Soc.*, 1958, *A*, **244**, 110; *A*, **246**, 91; *A*, **248**, 136; Neiman, Efremov, and Serdyuk, *Kinetika i Kataliz*, 1960, **1**, 345; Cartlidge and Tipper, *Proc. Roy. Soc.*, 1961, *A*, **261**, 388.

[5] Zeelenberg and Bickel, *J.*, 1961, 4014.

[6] Cullis, Hardy, and Turner, *Proc. Roy. Soc.*, 1959, *A*, **251**, 265.

[7] Cullis, Fish, and Turner, *Proc. Roy. Soc.*, 1962, *A*, **267**, 433.

[8] Kahler, Bearse, and Stoner, *Ind. Eng. Chem.*, 1951, **43**, 2777.

and MS 550 Silicone oil for C_3—C_6 hydrocarbons. A silica gel adsorption column was used for the analysis of C_1 and C_2 hydrocarbons and of permanent gases. Pinacolyl alcohol, t-butyl alcohol, hydrogen peroxide, and water were all detected among the products but could not be satisfactorily estimated by gas chromatography. Since some of the less volatile products, especially pinacolone, were strongly absorbed by all the usual lubricants, special heated grease-less taps were used throughout the analytical section of the apparatus.

RESULTS AND DISCUSSION

Figs. 1 and 2 show the principal condensable products formed during the slow oxidation of an equimolar 2,3-dimethylbutane–oxygen mixture at 380°. Reaction appears to take
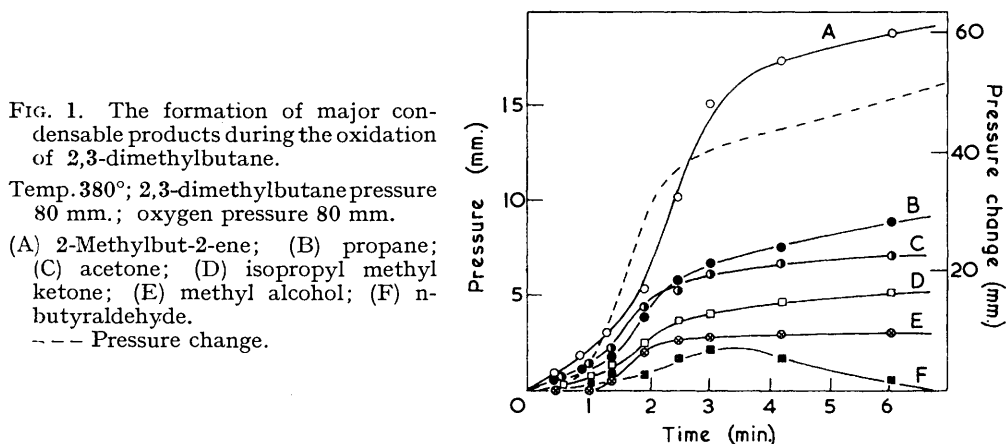

FIG. 1. The formation of major con-
densable products during the oxidation
of 2,3-dimethylbutane.

Temp. 380°; 2,3-dimethylbutane pressure
80 mm.; oxygen pressure 80 mm.

(A) 2-Methylbut-2-ene; (B) propane;
(C) acetone; (D) isopropyl methyl
ketone; (E) methyl alcohol; (F) n-
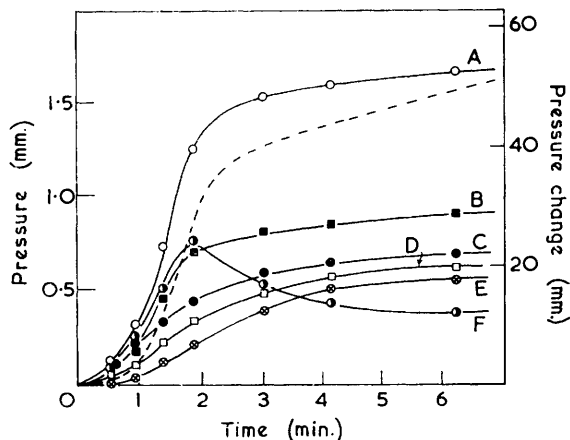butyraldehyde.
— — — Pressure change.

FIG. 2. The formation of minor con-
densable products during the oxidation
of 2,3-dimethylbutane. Conditions as
for Fig. 1.

(A) But-2-ene; (B) isopropyl alcohol;
(C) pinacolone; (D) isobutane; (E)
ethyl methyl ketone; (F) acetaldehyde.
— — — Pressure change.

place in three fairly well-defined stages. During an initial induction period the rates of formation of all products are small. This stage is followed by a period during which the reaction accelerates markedly and the rates of production of all intermediates except aldehydes reach a maximum. Finally a relatively slow reaction again takes place.

The most abundant condensable product is 2-methylbut-2-ene and this compound almost certainly arises from direct breakdown of the initially formed tertiary alkyl radicals:

$$\cdot CMe_2 \cdot CHMe_2 \longrightarrow Me_2C:CHMe + Me\cdot \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (1)$$
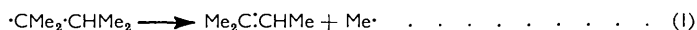
In the experimental conditions used in this work there will be quite rapid further oxidation of this olefin, and many of the oxygenated compounds detected are indeed known to be

products of its slow combustion.[7] The continuous increase with time of the concentration of 2-methylbut-2-ene (Fig. 1) and the roughly parallel production of this and most of the other condensable compounds (Figs. 1 and 2) suggest, however, that further reaction of the pentene with oxygen is not an important source of the other products. Instead, these compounds probably arise from other reactions of t-alkyl radicals which occur concurrently with (1). All the remaining products detected (except n-butyraldehyde and but-2-ene) can be accounted for—though not unequivocally—on the assumption that the alkyl radicals that are formed initially then react to give alkylperoxy-radicals and the corresponding alkyl hydroperoxide as a result of the well-known sequence:

$$R\cdot + O_2 \longrightarrow RO_2\cdot$$
$$RO_2\cdot + RH \longrightarrow RO\cdot OH + R\cdot$$
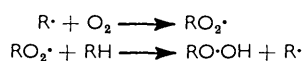
Nevertheless the exact modes of formation of the smaller product molecules can only be established with certainty with the aid of isotopic tracer techniques.

The formation of appreciable amounts of pinacolone (Fig. 2) and pinacolyl alcohol is of special interest inasmuch as the products contain the same number of carbon atoms as 2,3-dimethylbutane and presumably arise therefore directly from the original fuel molecule. The structures of both compounds are, however, such that rearrangement involving migration of a methyl group must have taken place in one of the intermediate species leading to their formation.

Although more than one reaction scheme will account for the production of pinacolone, the most likely route involves rearrangement of a t-alkylperoxy-radical, hydrogen transfer from carbon to oxygen:

$$Me_2C\langle^{O\cdot O\cdot}_{CHMe_2} \longrightarrow Me_2C\langle^{O\cdot OH}_{CMe_2\cdot} \qquad \cdots \cdots \cdots \quad (2)$$
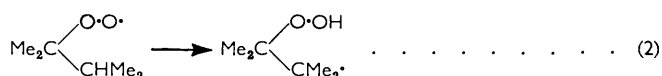
being followed by migration of a methyl group from the α- to the β-carbon atom and simultaneous fission of the O–O bond:

$$\longrightarrow Me\cdot CO\cdot CMe_3 \qquad \cdots \cdots \cdots \cdots \quad (3)$$
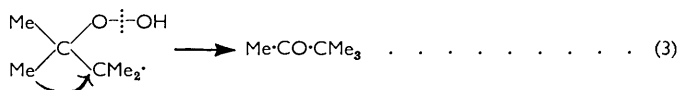
In the formation of pinacolyl alcohol, the t-alkylperoxy-radical probably first forms the corresponding hydroperoxide by intermolecular abstraction of hydrogen. Fission across the O–O bond, followed by isomerisation of the resulting alkoxy-radical, involving the migration of both hydrogen and a methyl group, would lead to a species which could to some extent stabilise itself by hydrogen abstraction to yield pinacolyl alcohol.
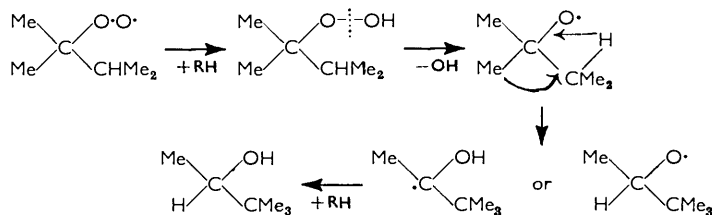
Alternatively the isomerisation might, of course, take place at the alkyl-radical stage, but no other example has yet been reported of alkyl-radical rearrangement involving 1,2-methyl transfer.[9] On the other hand, several instances are known where such transfer takes place in small oxygenated radicals.[5,6,7,10]

It is significant that studies of the slow oxidation of 2,2-dimethylbutane in comparable conditions show that, although a wide variety of small hydrocarbon and oxygenated product

[9] Cf. Kossiakoff and Rice, *J. Amer. Chem. Soc.*, 1943, **65**, 590.

[10] Cvetanovic, *Canad. J. Chem.*, 1958, **36**, 623.

molecules are formed, no pinacolone or pinacolyl alcohol can be detected.[11] Thus, although these two compounds have the same carbon skeleton as 2,2-dimethylbutane, they cannot be formed from it directly. The absence of tertiary (or secondary) CH groups in the α-position evidently makes it impossible for the alkylperoxy-radical, $Me_3C \cdot CHMe \cdot O \cdot O \cdot$, to stabilise itself by internal hydrogen abstraction by a reaction analogous to (2). Without this stabilisation, this peroxy-radical suffers extensive C–C bond fission and no stable C_6 oxygenated products can be formed from it.

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[11] Cf. Rust and Collamer, *J. Amer. Chem. Soc.*, 1954, **76**, 1055.