

# RADICAL REARRANGEMENT IN GAS-PHASE OXIDATION AND RELATED PROCESSES

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**Introduction.**—The reactions of organic molecules in the gas phase and in non-polar solvents often involve free-radical intermediates. Several modes of further reaction of such intermediates, including recombination, disproportionation, decomposition, displacement, and addition are often possible and the natures and amounts of the products formed during autoxidation, gaseous oxidation, and pyrolysis depend on the relative rates of these competing processes (*e.g.*, ref. 1). Recent work has established that a further important reaction of the free radicals produced in such systems is intramolecular rearrangement or isomerisation. Rearrangement reactions of common radical species have important kinetic, mechanistic, and preparative applications and are of increasing interest, particularly in the oxidation field. It is the aim of this Review to classify and discuss recent work on these reactions.

**General Characteristics of Radical Reactions.**—Radical reactions do not involve, in general, ionic or highly polarised species. They are insensitive therefore to the ionising power of media and take place quite similarly in the gas phase and in solution. Although their reactions in solution are usually studied in non-ionising solvents, this is not because radical reactions do not occur in ionising solvents but because these solvents encourage the occurrence of competing ionic processes. Similarly, radical reactions are insensitive to acid- and base-catalysis, but are catalysed by light and by radical sources such as peroxides, particularly when the radical reaction is a chain process. Free-radical chains are inhibited or retarded by stable radicals such as nitric oxide and diphenylpicrylhydrazyl and by substances such as amines, quinones, and aromatic polynitro-compounds, which react readily with free radicals to produce relatively stable radicals. Radical reactions are also sensitive to chain-termination processes such as destruction of active centres at the walls of the vessel.

The concepts of activation energy, frequency factor, and transition complex and the effects of "resonance" stabilisation and strain energy apply to radical reactions just as they do to molecular and ionic processes. Measurement and calculation of bond energies in free radicals and in the corresponding saturated molecules shows that, in general, the former are lower. The presence of an odd electron in a molecule has a weakening effect on the surrounding bonds and this phenomenon accounts for the ease of radical decomposition, disproportionation, and rearrangement reactions.

**Radical Rearrangements.**—Radical isomerisation reactions, or rearrange-

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<sup>1</sup> Cullis, *Chemistry and Industry*, 1962, 23.

ments, can be represented as an attack by the free valency of the radical on some other bond in the radical. These reactions occur by intramolecular transfer of an atom or group, usually the hydrogen atom, and an active centre migration. They thus involve the breaking of one  $\sigma$ -bond and the formation of another  $\sigma$ -bond and may therefore be compared with radical substitution (displacement) reactions but contrasted with decomposition reactions in which one  $\sigma$ -bond is broken and one  $\pi$ -bond formed. From this point of view, then, isomerisation may be regarded as intramolecular substitution. (Certain ring-opening isomerisation reactions involve the breaking of a  $\sigma$ -bond and the formation of a  $\pi$ -bond.)

Kinetically, the isomerisation reactions of free radicals are unimolecular, the rate being given by the expression

$$r_i = 10^{13} [\text{R}\cdot] \exp(-E_1/RT)$$

which may be compared with the rate of a substitution reaction between  $\text{R}\cdot$  and a molecule  $\text{M}$ :

$$r_s = 10^{-10} [\text{R}\cdot] [\text{M}] \exp(-E_2/RT)$$

(The values quoted for frequency factors,  $10^{13} \text{ sec.}^{-1}$  for a unimolecular reaction and  $10^{-10} \text{ cm.}^3 \text{ molecule}^{-1} \text{ sec.}^{-1}$  for a bimolecular reaction, are acceptable mean values. The apparent wide difference between these two values arises merely from the different units employed. The rates,  $r_i$  and  $r_s$ , have the same units,  $\text{molecules cm.}^{-3} \text{ sec.}^{-1}$ , as the bimolecular equation involves two concentration terms and the unimolecular equation only one.)

Comparison of these equations indicates the conditions under which isomerisation will compete successfully with substitution. At atmospheric pressure,  $[\text{M}] \simeq 10^{19} \text{ molecules/ml.}$ , giving

$$r_i/r_s = 10^4 \exp[-(E_1 - E_2)/RT]$$

If  $E_1 = E_2$ , then, isomerisation will be *ca.*  $10^4$  times as rapid as substitution. However, an important consideration in isomerisation reactions is the direction of approach of the free valency to the axis of the  $\sigma$ -bond which breaks. When an atom  $\text{A}$  attacks a diatomic molecule  $\text{BC}$ , the probability of reaction is greatest when the three atoms are collinear. As the angle of approach is increased, the activation energy increases; rough quantum-mechanical calculations indicate that the activation energy for perpendicular approach is approximately double that for collinear approach. In isomerisation, collinear approach is most unlikely and  $E_1$  is, in general, considerably greater than  $E_2$  for the corresponding intermolecular (substitution) reaction. At low temperatures, then,  $E_1$  will not be satisfied, and the exponential term will predominate, substitution occurring. At higher temperatures, this energy requirement is fulfilled and the pre-exponential factor predominates, isomerisation occurring. This requirement is reflected in the size of the "rings" involved in the transition complexes in isomerisation reactions. One would expect an optimum ring size corresponding to

low-angle approach, and indeed 7-, 6-, and 5-membered rings are most common, although 4-membered rings have also been postulated quite frequently.

Free-radical isomerisation is therefore favoured by high temperature, and by low pressure (when  $[M]$  is small, lowering  $r_s$ ). Under such conditions, it occurs in a wide variety of systems. Among the most important of these is the fuel-oxygen system, in which the noteworthy free-radical species are alkyl radicals, alkylperoxy-radicals, alkoxy-radicals and, in the case of unsaturated fuels, certain biradicals. The rearrangement reactions of these four species lead to several interesting types of compound, including hydrocarbons, carbonyl compounds, alcohols and acids with carbon skeletons different from that of the original organic molecule, *O*-heterocycles, dihydroperoxides, and cyclic peroxides, and under favourable conditions the yields of these can be quite high. As oxidation by molecular oxygen is inexpensive (particularly in the gas phase), isomerisation may become an economically attractive route for the synthesis of unusual products. As several of these products are effective chain-branching agents, the occurrence of isomerisation in such systems is mechanistically important and in several cases determines the overall rate and course of oxidation. For example, alkylperoxy-radical rearrangement is believed to lead to low-temperature ignition or "knocking" during combustion of hydrocarbon fuels.

Of the four radical species mentioned, alkyl radicals and alkylperoxy-radicals are the most important, being produced by the primary chain process during the oxidation of hydrocarbons, and as in the presence of oxygen the reaction



occurs rapidly, alkyl radical isomerisation is then infrequent. Alkylperoxy-radical isomerisation is therefore the most frequent rearrangement reaction in fuel-oxygen systems, alkyl radical isomerisation occurring extensively when oxygen is absent (*e.g.*, during pyrolysis). The features of the isomerisation of alkyl, alkylperoxy- and alkoxy-radicals, and of related biradicals, are discussed later, and preparative, kinetic, and mechanistic applications of these reactions are given.

### 1. Alkyl-radical Rearrangement

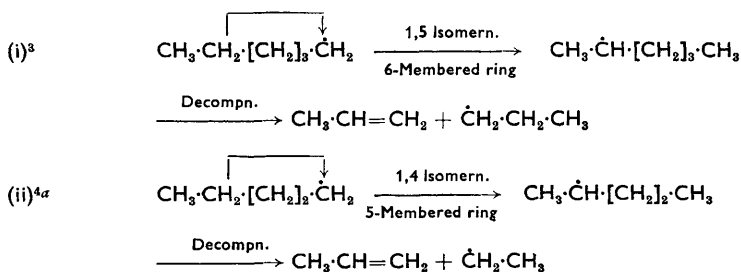
The rearrangement reactions of alkyl radicals may be divided into three classes, involving respectively intramolecular transfer of a hydrogen atom (in which one C-H bond is broken and one formed), transfer of an alkyl group (in which one C-C  $\sigma$ -bond is broken and one formed) and ring-opening (in which no group is transferred but a C-C  $\sigma$ -bond which is part of a ring is broken and a C-C  $\pi$ -bond is formed).

(a) **Transfer of Hydrogen.**—The occurrence of hydrogen transfer in alkyl radicals has been established for many years and can be followed

either by recombination or, more usually, by decomposition of the rearranged radical produced. It is well illustrated by experiments on the exchange of deuterium with alkyl radicals. For example, the exchange of deuterium with  $\text{Me}_2\text{CH}\cdot\dot{\text{C}}\text{H}_2$ ,  $\text{Et}\cdot\dot{\text{C}}\text{H}_2$ , and cyclo- $\text{C}_6\text{H}_{11}\cdot$  occurs readily,<sup>2</sup> producing radical recombination products which are deuterated to extents as great as 50%. Exchange in saturated molecules does not occur under these conditions. Moreover, the free valency of an alkyl radical can assist exchange in its immediate vicinity only, so the extent of exchange shows that the free valency is mobile, *i.e.*, that isomerisation occurs.

Hydrogen transfer may be classified according to the number of members in the "ring" of the transition complex involved, *e.g.*, 1,2 isomerisation (3 members), 1,3 isomerisation (4 members), etc. The relative concentrations of deuterium in the various skeletal positions after exchange<sup>2</sup> show that 1,3 isomerisation is much more common than 1,2 isomerisation. In cases such as  $\text{Me}_2\text{CH}\cdot\dot{\text{C}}\text{Me}_2$ , the 1,3 isomerisation of which must involve primary hydrogen and would therefore be markedly endothermic, little exchange takes place.

Isomerisation involving larger "rings", of five or more members, is in turn easier than 1,3 isomerisation, having a lower activation energy. This illustrates the general ease of 1,4 and, especially, 1,5 intramolecular H-transfer. Transfer of hydrogen around such rings occurs readily above 250°C in n-alkyl radicals containing five carbon atoms or more, being a unimolecular reaction with  $E_A \leq 9$  kcal./mole. Competing reactions such as *intermolecular* hydrogen abstraction and direct decomposition are slow by comparison. Rearrangement is usually followed by decomposition to an olefin and a simpler alkyl radical, *e.g.*,



Much of the important information on rearrangement of n-alkyl radicals has been obtained from studies of radical addition to olefins.<sup>4</sup> For example, in the addition to ethylene of methyl radicals, which produces over 50% of propene, the 1,4 isomerisation of the pent-1-yl radical to the pent-2-yl radical [*e.g.*, (ii) above] is an important process, and similar isomerisation

<sup>2</sup> Voevodskii, Lavrovskaya, and Mardaleishvili, Symposium on Chemical Kinetics, Catalysis and Reactivity, Acad of Sci., Moscow, 1956, 40.

<sup>3</sup> Rice and Kossickoff, *J. Amer. Chem. Soc.*, 1943, **65**, 590.

<sup>4</sup> Gordon and McNesby, *J. Chem. Phys.*, (a) 1959, **31**, 853; (b) 1960, **33**, 1882.

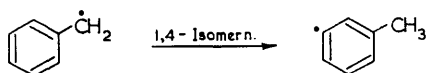
of the hept-1-yl radical, formed by the addition of a further molecule of ethylene, also participates. The prominence of these reactions has been substantiated by using trideuteromethyl radicals.

In the case of smaller *n*-alkyl radicals ( $C_4$  or less) isomerisation of the 1-alkyl radical to the 2-alkyl radical must involve an activated complex with a ring of four members or less, and no appreciable isomerisation of  $CH_3 \cdot [CH_2]_2 \cdot CH_2$  occurs under conditions where higher 1-alkyl radicals isomerise readily.<sup>5</sup> Under more energetic conditions, however, the occurrence of 1,3 isomerisation of the 1-butyl radical is established<sup>6</sup> (cf. ref. 7) and has a low pre-exponential factor and an activation energy of 27 kcal./mole, *i.e.*, three times that of transfer around larger rings.

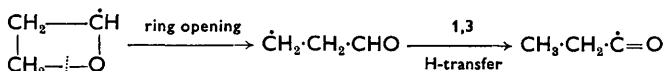
Isomerisation of the isopropyl radical is necessarily restricted to 1,2 H-transfer, giving the *n*-propyl radical, but occurs during isopropyl radical decomposition<sup>8</sup> and the photolysis of di-isopropyl ketone in the presence of metals.<sup>9</sup>

To summarise, the occurrence of 1,2 and 1,3 isomerisation reactions of small alkyl radicals is established, but in larger alkyl radicals these processes are swamped by the energetically-favoured transfer of hydrogen around five- or six-membered rings, *i.e.*, 1,4 and 1,5 intramolecular H-transfer.

Such isomerisation is not restricted to simple alkyl radicals but is an important process during the decomposition of a variety of substances. Thus intramolecular abstraction of a hydrogen atom of the benzene ring of an aryl radical occurs in much the same way as in an alkyl radical, *e.g.*,<sup>10</sup>



Studies of the peroxide-induced reactions of cyclic ethers (oxirans, oxetans, tetrahydrofuran, and tetrahydropyran) with oct-1-ene<sup>11</sup> have established the general occurrence of isomerisation of a substituted alkyl radical to an acyl radical simultaneously with, or very rapidly after, ring opening, *e.g.*,



The resulting acyl radical adds to the oct-1-ene present and the adduct  $C_2H_5 \cdot CO \cdot CH_2 \cdot \dot{C}H \cdot [CH_2]_5 \cdot CH_3$  abstracts a hydrogen atom from a further

<sup>5</sup> McNesby, Gordon, and Drew, *J. Chem. Phys.*, 1956, **24**, 1260.

<sup>6</sup> Kerr and Trotman-Dickenson, *J.*, 1960, 323, 1602.

<sup>7</sup> Sefton and Leroy, *Canad. J. Chem.*, 1956, **34**, 41.

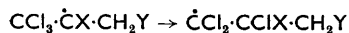
<sup>8</sup> Heller and Gordon, *J. Phys. Chem.*, 1958, **62**, 709; Kerr and Trotman-Dickenson, *Trans. Faraday Soc.*, 1959, **55**, 572, 921.

<sup>9</sup> Glazebrook and Pearson, *J.*, 1936, 1777.

<sup>10</sup> Hickenbottom, *Nature*, 1936, **142**, 830.

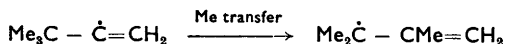
<sup>11</sup> Wallace and Gritter, *J. Org. Chem.*, 1961, **26**, 282, 5256; 1962, **27**, 3067; *Tetrahedron*, 1963, **19**, 657.

molecule of cyclic ether, conferring linear chain character on the overall addition reaction. Similar alkyl-acyl isomerisation accompanies ring-opening during the pyrolysis of ethylene oxide.<sup>12</sup> Again, in the peroxide-catalysed addition of halogen compounds to halogeno-olefins and in the ultraviolet light-initiated rearrangement of halogeno-olefins, isomerisation of halogeno-alkyl radicals occurs by 1,2 transfer of a halogen atom,<sup>13</sup> giving yields of rearranged products approaching 100%, e.g.,



where X is an alkyl radical or a halogen atom and Y is a halogen atom.

(b) **Transfer of Alkyl Groups.**—Isomerisation of alkyl radicals by intramolecular transfer of an alkyl group is much less common than by transfer of hydrogen. The best-known example of such group transfer is the rearrangement of an  $\alpha$ -disubstituted vinyl radical to the corresponding  $\alpha$ -monosubstituted allyl radical, e.g.



which occurs during decomposition of 1,1-disubstituted alkenes, particularly when the substituents are tertiary alkyl groups<sup>14</sup> [e.g.,  $(\text{Me}_3\text{C})_2\text{C} = \text{CH}_2$ ].

1,2 Migration of alkyl or aryl groups occurs during the decomposition of azo-compounds:<sup>15</sup>



although this process does not affect the rate-determining step of the decomposition (*i.e.*, the breaking of the C-N bond). A similar 1,2 migration of a methyl group occurs during the pyrolysis of neopentyl chloride, the major (75%) mode of decomposition producing hydrogen chloride and an equilibrium mixture of the three isomeric methylbutenes. It has been suggested<sup>16</sup> that dehydrochlorination occurs *via* a free-radical intermediate and provides an example of a Wagner-Meerwein type of rearrangement in the gas phase. Analogous rearrangement during decomposition of gaseous neopentyl chloroformate appears, however, to have a polar mechanism.<sup>17</sup>

(c) **Ring-opening and  $\pi$ -Bond Formation.**—In strained ring systems, free-radical isomerisation by ring-opening and double-bond formation gives rise to some interesting products. In solution, although such free-radical

<sup>12</sup> Lossing, Ingold, and Tickner, *Discuss. Faraday Soc.*, 1953, 14, 34.

<sup>13</sup> Nesmeyanov, Freidlina, and Zakharin, *Doklady. Akad. Nauk S.S.S.R.*, 1951, 81, 199; Nesmeyanov, Freidlina, and Kost, *Quart. Rev.*, 1956, 10, 330; *Tetrahedron*, 1957, 1, 241; Freidlina, Kost, and Khorlina, *Russian Chemical Reviews*, 1962, Part I, p. 1.

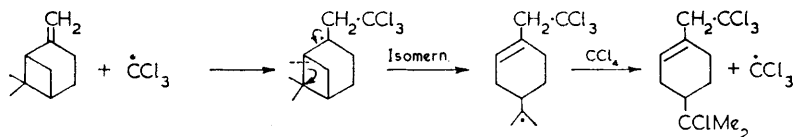
<sup>14</sup> Nasarov, *Ber.*, 1937, 70, B, 606, 617.

<sup>15</sup> Overberger and Gainer, *J. Amer. Chem. Soc.*, 1958, 80, 4561.

<sup>16</sup> Maccoll and Swinbourne, *Proc. Chem. Soc.*, 1960, 409.

<sup>17</sup> Lewis and Herndon, *J. Amer. Chem. Soc.*, 1961, 83, 1961.

reactions are less common than those of the corresponding carbonium ions, they occur during reactions such as addition of halogenomethanes to olefins. In the free-radical chain addition of carbon tetrachloride to  $\alpha$ -pinene, for example, the following mode of chain propagation is important.<sup>18</sup>



The energy needed for such rearrangement is probably provided by the relief of strain due to the rupture of the 4-membered homocyclic ring of the original pinene skeleton.

The thermal decomposition in solution in n-hexadecane or diphenyl ether of the 2-bornyl radical (I) provides an example of isomerisation in which ring cleavage is followed by recyclisation.<sup>19</sup> The 2-bornyl radical is formed during the reaction of camphane-2-carboxyaldehyde with t-butyl hydroperoxide or, at higher temperatures, by thermal decomposition of 2,2'-bisazocamphane (II).

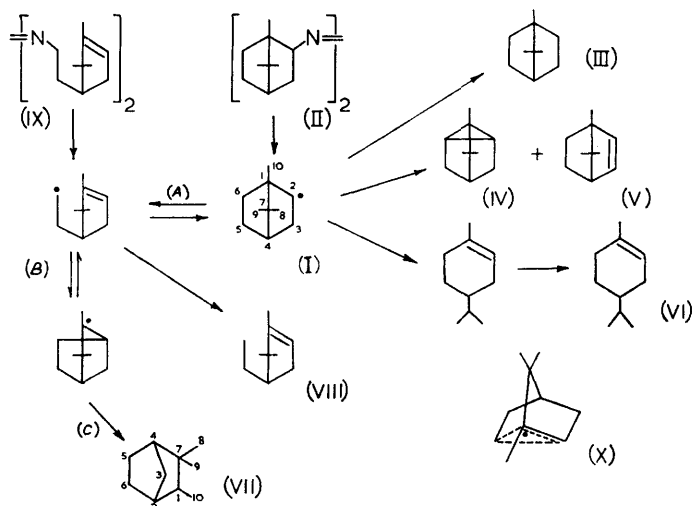
At temperatures of *ca.* 150°C, no rearrangement of (I) occurs. Intermolecular H-abstraction gives bornane (III) (the major product) and disproportionation to tricyclene (IV) and bornene (V) occurs. At higher temperatures (255°–290°) however, ring opening followed by intermolecular H-abstraction gives *p*-menthene (VI), and 2,3,3-trimethylnorbornane (isocamphane) (VII) is produced by *intramolecular alkyl-group shift*. It is considered that three steps are involved in the production of isocamphane: ring-opening and  $\pi$ -bond formation (*A*) is followed by ring closure in the opposite sense (*B*) and, in turn, intermolecular H-abstraction (*C*). The occurrence of step (*A*) is supported by the production of (VI) as this must necessarily involve ring-opening and  $\pi$ -bond formation. Moreover, the olefin 4-ethyl-1,5,5-trimethyl-cyclopent-1-ene (VIII) has been tentatively identified in the products. Direct evidence that step (*B*) occurs is provided by the thermal decomposition of the azo-compound (IX) which gives products qualitatively similar to those from (II). The quantitative distribution of products depends however on the starting material and the isocamphane formed is a mixture of both isomers. The cleavage-recyclisation mechanism of rearrangement to isocamphane, as depicted below, is therefore favoured rather than isomerisation *via* a mesomeric bridged radical (X) as the sole intermediate, because the abstraction of hydrogen by this bridged radical would be stereospecific and would also be expected to give the same product distribution from both azo-compounds (II and IX).

The fact that *p*-menthene and isocamphane are formed at high tempera-

<sup>18</sup> Oldroyd, Fisher, and Goldblatt, *J. Amer. Chem. Soc.*, 1950, **72**, 2407.

<sup>19</sup> Berson, Olsen, and Walia, *J. Amer. Chem. Soc.*, 1960, **82**, 5000; 1962, **84**, 3337.

tures only is also consistent with this mechanism, as step (A) will have an activation energy substantially higher than those of disproportionation of and intermolecular H-abstraction by the 2-bornyl radical.



## 2. Alkylperoxy-radical Rearrangement

The occurrence of isomerisation has been established for alkylperoxy-radicals of a wide variety of structures, and is a most important reaction during many oxidation processes, competing with hydroperoxide formation by *intermolecular* hydrogen abstraction. Isomerisation occurs by transfer to the oxygen atom having the unpaired electron of an atom or group from some other part of the molecule. Two prerequisites for the occurrence of such a reaction are that, first, the lifetimes of  $\text{RO}_2\cdot$  radicals are sufficiently long to show that they survive many collisions with other molecules, so that there might be time for the radical to attain a conformation suitable for the occurrence of isomerisation, and that, secondly, the relatively high activation energy for isomerisation must be satisfied. McDowell<sup>20</sup> has shown that  $\text{RO}_2\cdot$  radicals do indeed survive many collisions and it has been suggested<sup>21</sup> that they may be endowed with considerable excess of vibrational energy, supplied by the exothermicity of the alkyl radical-oxygen addition reaction, which could contribute to the activation energy required.

The simplest alkylperoxy-radical is  $\text{CH}_3\text{OO}\cdot$ , which is formed during the oxidation of methane by



<sup>20</sup> McDowell, *Discuss. Faraday Soc.*, 1951, 10, 323.

<sup>21</sup> (a) Small and Ubbelohde, *J. Appl. Chem.*, 1953, 3, 193; (b) Ubbelohde, "Six lectures on the basic combustion process", Ethyl Corporation, Detroit, 1954.



and decomposes by



It is evident that step (2) must involve isomerisation by transfer of H from C to O, *viz.*<sup>22</sup>



and this process has, therefore, a high activation energy (*ca.* 20 kcal./mole). Nevertheless, in the oxidation of methane,<sup>22a</sup> reaction (2) follows reaction (1) rapidly, for

$$\text{Rate of (2)} = 10^{13}[\text{CH}_3\cdot\text{O}\cdot\text{O}\cdot]e^{-20/RT}$$

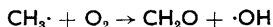
$$\text{and Rate of (1)} = 10^{-13}[\text{O}_2][\text{CH}_3\cdot]e^0$$

(the experimental frequency factor of  $10^{-13}$  showing that (1) occurs either at binary collisions with a steric factor of  $10^{-3}$  or, more probably, at every ternary collision). Hence, at 700°K, when the partial pressure of oxygen is 157 mm. Hg.,

$$\text{Rate of (2)} = a_2[\text{CH}_3\cdot\text{O}\cdot\text{O}\cdot], \text{ where } a_2 = 6.3 \times 10^6$$

$$\text{and Rate of (1)} = a_1[\text{CH}_3\cdot], \text{ where } a_1 = 2.2 \times 10^5$$

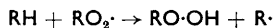
The reaction sequence is therefore usually represented as a single step:



For higher alkylperoxy-radicals also, this well-established mode of decomposition to a carbonyl compound and a hydroxyl radical must involve isomerisation by hydrogen transfer in order that  $\cdot\text{OH}$  may be formed.



The work of Fok and Nalbandyan<sup>22b</sup> on the photo-oxidations of methane, ethane, and propane illustrates the temperature dependence of such an isomerisation reaction. Below 100°C, peroxides are the only products of photo-oxidation, the substitution reaction

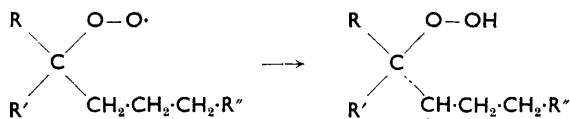


occurring, but above 100°C, aldehydes are produced also, by the above isomerisation and decomposition sequence. At higher temperatures still, this mode of reaction of  $\text{RO}_2\cdot$  occurs exclusively.

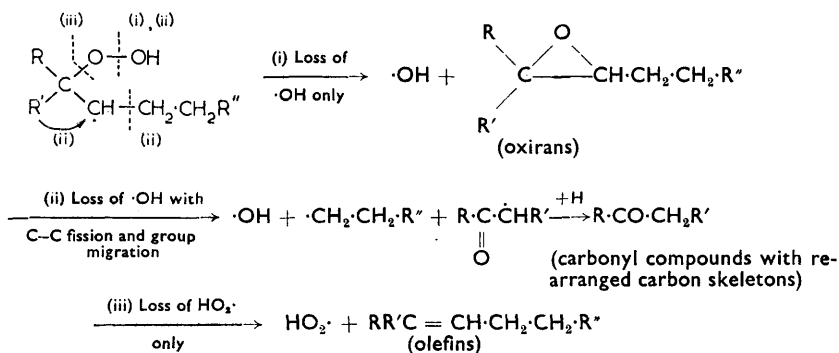
In more complex cases, several modes of isomerisation are possible and each of these may be followed by several decomposition reactions leading to a wide variety of products, many of which are diagnostic of the occurrence of isomerisation. The possibilities may be represented as follows:

<sup>22</sup> Fok and Nalbandyan, *Doklady. Akad. Nauk S.S.S.R.*, (a) 1952, **86**, 589; (b) 1953, **89**, 725; (c) Neiman, Eframov, and Serdyuk, *Kinetiki i Kataliz*, 1960, **1**, No. 3, 345; (d) Karmilova, Enikolopyan, and Nalbandyan, *Zhur. fiz. Khim.*, 1957, **31**, 851; 1960, **34**, 562.

(a) *Isomerisation by H-transfer.* Transfer of H from  $\alpha$ -C:



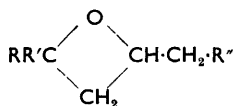
followed by decomposition



Transfer of H from  $\beta$ -C:

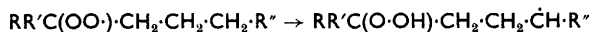


followed by decomposition by routes similar to (i) and (ii) (above), producing oxetans

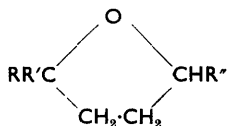


and carbonyl compounds  $\text{R}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{R}'$  respectively.

Transfer of H from  $\gamma$ -C:



followed by decomposition giving derivatives of tetrahydrofuran



and carbonyl compounds  $\text{R}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{R}'$ .

(b) *Isomerisation by group transfer.* For example,



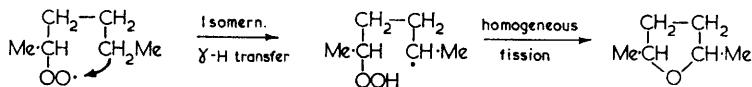
followed by decomposition by fission of the O-O link giving an alkoxy-radical and a carbonyl compound.

(c) *Isomerisation by ring opening.* This, which can be regarded as a special case of group transfer, is possible if R or R' has a ring structure.

Furthermore, when  $\text{RO}_2\cdot$  isomerisation occurs during hydrocarbon oxidation, the resulting radical is susceptible to further oxidative attack which may be followed by *intermolecular* hydrogen abstraction giving a dihydroperoxide, e.g.,  $\text{RR}'\text{C}(\text{O}\cdot\text{OH})\cdot\text{CH}_2\text{-CH}(\text{O}\cdot\text{OH})\cdot\text{CHR}''$ , the breakdown of which will produce  $\beta$ -dicarbonyls and other disubstituted hydrocarbons. These possibilities will now be considered in turn.

(a) *Isomerisation by Transfer of a Hydrogen Atom.*—(i) *Followed by simple decomposition to O-heterocycles.* Intramolecular H-transfer followed by homogeneous fission of the O–O bond without fission of any other bond gives a biradical in which one unpaired electron is sited on oxygen and the other on carbon. This biradical cyclises, producing a stable or moderately stable O-heterocycle. The overall yields of such compounds, calculated as percentages of total hydrocarbon oxidation products, establish alkylperoxy-radical isomerisation as a reaction of major importance in fuel–oxygen systems and are sometimes sufficient to provide an attractive synthetic route.

The occurrence in combustion condensates of saturated furans and pyrans was first reported by Ubbelohde<sup>23</sup> who studied the n-pentane–oxygen system at 300°C; one of the earliest interpretations of such products in terms of alkylperoxy-radical isomerisation followed by loss of a hydroxyl group is due to Bailey and Norrish<sup>24</sup> who found 2,5-dimethyltetrahydrofuran in the products of oxidation of n-hexane in the cool-flame region, thus providing unambiguous evidence for the participation of the hex-2-ylperoxy-radical:



Smaller quantities of 2-methyltetrahydropyran, formed from the hex-1-ylperoxy or hex-2-ylperoxy-radical, and of an unknown ether boiling at 106°C were also detected. More recent work has confirmed the presence of these 5- and 6-membered heterocycles in combustion products. Tetrahydrofuran derivatives, in particular, have been found under a wide variety of conditions. For example, the n-hexane–air cool flame, stabilised in a tube,<sup>25</sup> produces 2-ethyltetrahydrofuran and both *cis*- and *trans*-tetrahydro-2,5-dimethylfuran, while the n-pentane–air system in an annular flow reaction vessel gives 2-methyltetrahydrofuran over a wide variety of temperature and reactant-ratio conditions,<sup>26</sup> the maximum yield being obtained between 450 and 500°C.

<sup>23</sup> Ubbelohde, *Proc. Roy. Soc.*, 1935, A, **152**, 354, 378.

<sup>24</sup> Bailey and Norrish, *Proc. Roy. Soc.*, 1952, A, **212**, 311.

<sup>25</sup> Kyriacos, Menapace, and Boord, *Analyt. Chem.*, 1959, **31**, 222.

<sup>26</sup> Chung and Sandler, *Combustion and Flame*, 1962, **6**, 295.

Oxetans (*O*-heterocycles with a four-membered ring) were discovered, in addition to tetrahydrofurans, among hydrocarbon combustion products by Rust and Collamer<sup>27</sup> who used infrared techniques to study the oxidation products of branched hydrocarbons, and showed that the products of combustion of 2,2,4-trimethylpentane contained tetrahydro-2,2,4,4-tetramethylfuran and 2-methyl-1-t-butyloxetan, while 2,2-dimethylbutane yielded 2,3,3-trimethyloxetan. The advent of gas chromatography enabled mixtures of *O*-heterocycles with 3-, 4-, 5-, and 6-membered rings to be analysed readily and, since 1959, several papers have established not only the formation of such compounds by oxidation of a wide variety of hydrocarbons, but also the production of mixtures of such compounds from a single hydrocarbon, illustrating the diversity of possible routes of alkylperoxy-radical rearrangement and breakdown. For example, the slow oxidation of isobutane in the gas phase<sup>28</sup> yields, in the second stage of the induction period, 2,2-dimethyloxiran (isobutene oxide), methyloxiran (propylene oxide), and 3-methyloxetan. Rearrangement by  $\alpha$ -H transfer of the t-butylperoxy-radical or the isobutylperoxy-radical followed by elimination of  $\cdot\text{OH}$  gives isobutene oxide; in the case of isobutylperoxy, two further possibilities occur,  $\beta$ -H transfer and loss of  $\cdot\text{OH}$  giving 3-methyloxetan, and group transfer [Section 2(b)] giving propylene oxide. Similarly, the slow combustion of neopentane<sup>29</sup> produces, by H-transfer in and decomposition of the neopentylperoxy-radical, 3,3-dimethyloxetan. In the cases of n-heptane and of n-hexane, no less than five oxygen heterocycles have been detected and estimated in the products of gaseous oxidation under specialised conditions,<sup>30</sup> n-hexane giving 2,5-dimethyltetrahydrofuran, 2-ethyltetrahydrofuran, 2-ethyl-4-methyloxetan, 2-n-propyloxetan, and 3-methyl-2-n-propyloxiran, and n-heptane giving 2-ethyl-5-methyltetrahydrofuran, 2-n-propyltetrahydrofuran, 4-methyl-2-n-propyloxetan, 3-ethyl-2-n-propyloxiran and 2-n-propyloxiran.

(ii) *Followed by C-C bond fission giving carbonyl compounds.* During the oxidation of hydrocarbons and their simple derivatives, carbonyl compounds may be produced in a variety of ways, notable among which is the breakdown of alkoxy-radicals. From analytical data alone it is often difficult to distinguish this reaction from alkylperoxy-radical rearrangement followed by decomposition involving carbon-carbon bond fission (a common phenomenon<sup>31</sup> in the decomposition of a wide variety of peroxidic species). Unambiguous evidence for a mode of formation involving rearrangement has been obtained however in several cases in which an alkyl group is transferred intramolecularly during decomposition. (Note that the original isomerisation of the *alkylperoxy-radical* still involves H-transfer).

<sup>27</sup> Rust and Collamer, *J. Amer. Chem. Soc.*, 1954, **76**, 1055.

<sup>28</sup> Zeelenberg, and Bickel, *J.*, 1961, 4014.

<sup>29</sup> Zeelenberg, *Rec. Trav. chim.*, 1962, **81**, 720.

<sup>30</sup> Jones and Fenske, *Ind. Eng. Chem.*, 1959, **51**, 262; Jones, Allendorf, Hutton, and Fenske, *J. Chem. Eng. Data*, 1961, **6**, No. 4, 620.

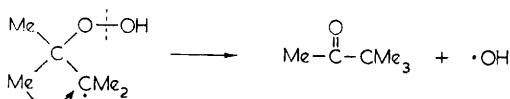
<sup>31</sup> Leffler, *Chem. Rev.*, 1949, **45**, 385.

The resulting carbonyl compound then has a *rearranged carbon skeleton* which could not be produced from the original fuel molecule without postulating isomerisation (or a very complicated and unlikely sequence of intermolecular processes).

For example, the pinacolone formed during the gaseous oxidation of 2,3-dimethylbutane<sup>32</sup> probably arises directly from the original fuel molecule as it has the same number of carbon atoms. The structures of the two compounds are, however, such that rearrangement involving 1,2 migration of a methyl group must have taken place at some intermediate stage. The most likely route involves rearrangement of a tertiary alkylperoxy-radical by hydrogen transfer from carbon to oxygen.



followed by migration of a methyl group to the  $\alpha$ -carbon atom and simultaneous fission of the O-O bond:

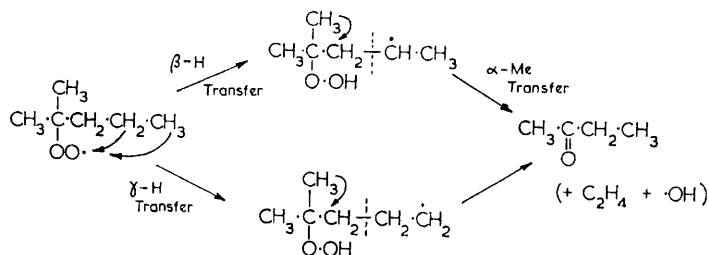


The intramolecular nature of such group transfers has been established by Cullis and his collaborators using <sup>14</sup>C-tracer techniques. The mechanism of formation of ketones (acetone, methyl n-propyl ketone, ethyl methyl ketone) during the slow combustion of 2-methylpentane has been elucidated by separation and degradation of the ketones formed from specifically-labelled hydrocarbons.<sup>33</sup> The oxygenated carbon atom of each ketone is always derived from the 2-position of the hydrocarbon. There can be little doubt that the acetone and methyl n-propyl ketone arise by breakdown of the tertiary alkoxy-radical  $\text{Pr}^n\text{Me}_2\text{C}\cdot\text{O}\cdot$  (cf. ref. 34). It is on the other hand somewhat more difficult to account for the formation of ethyl methyl ketone, which is a major product (*ca.* 13 moles/100 moles fuel consumed) and is therefore not formed by radical-radical interactions or other secondary processes. The specific activities of the samples of ethyl methyl ketone formed from 2-methylpentanes labelled in turn in the 2-, 3-, 4-, and 5-positions show that the four carbon atoms from which the ethyl methyl ketone is formed have the arrangement C-C(C)-C in the fuel. An intramolecular rearrangement producing a straight four-carbon chain must therefore be involved in the oxidation mechanism and almost certainly occurs in the 2-methylpent-2-ylperoxy-radical by internal hydrogen migration from the 4- (or possibly 5-) position, followed by  $\alpha$ -methyl transfer producing ethyl methyl ketone:

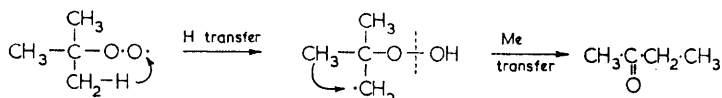
<sup>32</sup> Trimm and Cullis, *J.*, 1963, 1430.

<sup>33</sup> Cullis, Hardy, and Turner, *Proc. Roy. Soc.*, 1959, *A*, **251**, 265.

<sup>34</sup> Raley, Rust, and Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 88.



A similar isotopic study of the slow combustion and cool-flame oxidation of isobutane<sup>35</sup> has established further the intramolecular nature of the production of rearranged carbonyl compounds, providing strong evidence against substantial formation of ethyl methyl ketone from acetone by intermolecular methyl donation. In each of these two combustion regimes, [1,3-<sup>14</sup>C]acetone was added to an isobutane-oxygen mixture and the specific activity of the acetone present *after* combustion was compared with that of the ethyl methyl ketone formed. In the cool flame region, the formation of at least 98% of the large quantities of ethyl methyl ketone produced did not involve acetone, being consistent with



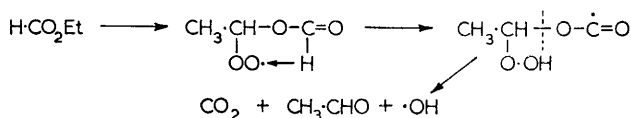
Similarly, this reaction is capable of accounting for *ca.* 75% of the much smaller concentration of ethyl methyl ketone produced during slow combustion. (The other 25% incorporated carbon-14, originating from acetone.) It was concluded that intramolecular rearrangement of the t-butylperoxy-radical occurred during slow combustion and was a reaction of considerable importance in the cool-flame oxidation of isobutane. The relative frequencies of this rearrangement and of intermolecular substitution followed by hydroperoxide decomposition giving acetone were 1:27 during slow combustion but *ca.* 20:1 under cool-flame conditions.

In cases where intramolecular H-transfer is followed by fission of a "skeletal" bond, but no intramolecular group transfer occurs, the products of alkylperoxy-radical rearrangement include carbonyl compounds, but these no longer have carbon skeletons containing atomic arrangements not present in the fuel molecule. The use of labelling is restricted therefore to isotopes of hydrogen, and this technique would introduce large kinetic isotope effects.<sup>36</sup> Much of the evidence for hydrogen transfer with skeletal-bond fission is therefore indirect, but kinetic and analytical studies have been substantiated by the use of scaled molecular models. As the separate occurrences of H-transfer (producing *O*-heterocycles) and of skeletal

<sup>35</sup> Cullis, Fish, and Trimm, *Proc. Roy. Soc.*, 1963, *A*, 273, 427.

<sup>36</sup> Bigeleisen and Wolfsberg, "Advances in Chemical Physics", Interscience, New York, 1958, Vol. 1, p. 15.

fission have been substantiated fully, there seems little reason to doubt their occurrence in the same system. Examples are known of the production of carbonyl compounds by such rearrangement of alkylperoxy-radicals derived from a wide variety of fuel molecules, including alkanes,<sup>37</sup> formates,<sup>38</sup> and amines.<sup>39</sup> During the oxidation of formates, for instance, 1,5-intramolecular H-transfer followed by fission of a skeletal C–O bond (as well as the usual homogeneous fission of the peroxidic O–O bond) is of major importance,<sup>38</sup>

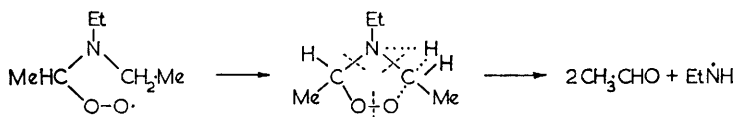


acetaldehyde being the only organic product in a given temperature region. Esters of higher organic acids (acetates, propionates, etc.) do not exhibit an analogous temperature region, possibly because in these cases H-transfer must involve a ring of at least seven members, *i.e.*, must be 1,*n*H-transfer where  $n \geq 6$ .

Particularly strong support for such a mechanism has been obtained during studies of the oxidation of tertiary amines.<sup>39</sup> There is a striking similarity in behaviour between triethylamine and *N*-methyldiethylamine on the one hand and between *N*-ethyl dimethylamine and trimethylamine on the other. In the former cases, an overall reaction takes place producing acetaldehyde and a primary amine:



and this becomes the sole process during the later stages of reaction, as it is not inhibited by the oxidation products. The peroxy-radical involved in the oxidation of triethylamine is  $\text{CH}_3\text{-CH}(\text{OO}\cdot)\text{-NEt}_3$ , *intermolecular* H-abstraction by which, followed by decomposition, will give predominantly acetaldehyde and diethylamine, monoethylamine production involving the simultaneous fission of *two* C–N bonds. Decomposition of the  $\text{RO}_2\cdot$  radical can only lead to the production of monoethylamine if there is some form of intramolecular attack, followed by decomposition, *viz.*,



and stabilisation of the resulting radical  $\text{EtNH}\cdot$  by abstraction of hydrogen from further triethylamine. This involves intramolecular rearrangement of

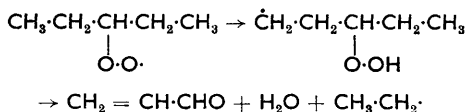
<sup>37</sup> Semenov, "Some Problems of Chemical Kinetics and Reactivity", Pergamon Press, London, 1958, Vol. 1, p. 100.

<sup>38</sup> Fish and Waris, *J.*, 1963, 820.

<sup>39</sup> Cullis and Waddington, *Proc. Roy. Soc.*, (a) 1958, *A*, 244, 110; (b) 1958, *A*, 246, 91; (c) 1958, *A*, 248, 136.

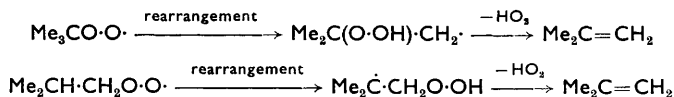
$RO_2\cdot$  in which H is "pushed" from C to N. A similar reaction, producing a radical  $CH_3NH\cdot$ , is capable of explaining the similar course of *N*-methyl-diethylamine oxidation. In the cases of *N*-ethyl-dimethylamine and trimethylamine, however, the peroxy-radical formed by the primary oxidation chain does not undergo such intramolecular attack to yield primary amine. The reason for this may be steric; it has been suggested<sup>39a,b</sup> that in the peroxy-radical  $CH_3\cdot CH(OO\cdot)\cdot NR'R''$  the outer oxygen atom will approach closely a hydrogen atom on the  $\alpha$ -C of  $R'$  if  $R'$  is an ethyl group but not if  $R'$  is a methyl group. The lower bond strength of secondary C-H than of primary C-H may also, however, be a contributing factor. Intramolecular attack is difficult, then, unless the original amine contains *two* ethyl groups. Hence the occurrence of this  $RO_2\cdot$  isomerisation provides a consistent and simple explanation of the differences in oxidation courses between the two pairs of tertiary amines.

A slight variation in the course of decomposition following hydrogen transfer in an alkylperoxy-radical has been postulated<sup>26</sup> to account for the production of acrolein during the oxidation of *n*-pentane, both C-C and C-H bond fission accompanying O-O bond fission resulting in the elimination of water and an alkyl radical:



Similarly, initial attack at the  $C_{(2)}$  atom of *n*-pentane and isomerisation by transfer of H from  $\beta$ -C is capable of explaining the production of crotonaldehyde, water and a methyl radical being eliminated.<sup>40</sup>

(iii) *Followed by loss of  $HO_2\cdot$  giving olefins.* Rearrangement of an alkylperoxy-radical by transfer of H from  $\alpha$ -C produces a radical  $RR'C(OOH)\cdot CHR''$  in which the proximity of the unpaired electron weakens the C-O bond. A hydroperoxy-radical may therefore be lost, yielding a biradical which is an excited state of an olefin  $RR'C=CHR''$ . Production of olefins by this route is responsible for the formation of isobutene as the major product during the induction period of the gaseous oxidation of isobutane:<sup>28</sup>



(iv) *Followed by further attack giving disubstituted products.* Disubstituted products may be formed by further oxidative attack at the position from which hydrogen has been transferred during rearrangement.

<sup>40</sup> Malmberg, Smith, Bilger, and Bobbitt, "Fifth Symposium on Combustion", Reinhold, New York, 1958, p. 385.

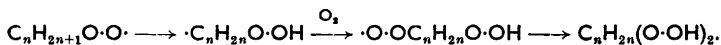


One of the fullest studies of the reaction has been made on the liquid-phase oxidation of 5-methylnonane.<sup>41</sup> At 90°C, initial attack on the hydrocarbon by oxygen removes tertiary hydrogen 19 times as frequently as secondary hydrogen, which is removed in turn 4 times as frequently as primary hydrogen. The predominant resulting alkyl radical is therefore  $\text{Bu}^n\cdot\text{C}(\text{Me})\cdot\text{Bu}^n$  and the peroxy-radical formed by subsequent addition of oxygen is  $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}(\text{Me})(\text{OO}\cdot)\cdot\text{Bu}^n$  in which there are three possible modes of transfer of secondary hydrogen, from the  $\alpha$ ,  $\beta$ , and  $\gamma$  carbon atoms. Further oxidative attack at these positions will lead to three disubstituted 5-methylnonanes, these being 4,5-, 3,5-, and 2,5- disubstituted products respectively. The autoxidation products were reduced by lithium aluminium hydride, converting monosubstituted products into alcohols and the disubstituted products (which were presumably dihydroperoxides) into the corresponding diols. These resulting hydroxy-compounds were analysed gas-liquid chromatographically showing that the ratios of diols produced were

$$2,5\text{-diol} : 3,5\text{-diol} : 4,5\text{-diol} = 8:4:1.$$

Thus transfer of H from  $\gamma$ -C is the most frequent mode of rearrangement of the 5-methylnon-5-ylperoxy-radical, while transfer of H from  $\beta$ -C is more frequent than from  $\alpha$ -C.

*Dihydroperoxides.*—The formation of dihydroperoxides by further oxidative attack following intramolecular rearrangement of  $\text{RO}_2\cdot$  has been established both in solution and in the gas phase.



In solution, Rust<sup>42</sup> has studied the formation of dihydroperoxides by autoxidation of dimethyl substituted n-alkanes (2,3-dimethylpentane, 2,4-dimethylpentane, 2,5-dimethylhexane, and 2,6-dimethylheptane) and it is interesting to compare his findings with those of Arndt and his collaborators.<sup>41</sup> By comparing the above range of branched hydrocarbons, each of which has two tertiary hydrogen atoms, Rust showed that transfer of H from  $\beta$ -C was most frequent; considerable transfer of H from  $\gamma$ -C also took place but rearrangement involving  $\alpha$  or  $\delta$  C-H groups was of little or no significance. The yields of 2,4-dihydroperoxy-2,4-dimethylpentane from 2,4-dimethylpentane and of 2,5-dihydroperoxy-2,5-dimethylhexane from 2,5-dimethylhexane were each *ca.* 90% of the total autoxidation product (cf. ref. 43), illustrating the high efficiency of intramolecular oxidation when the hydrogen involved in the rearrangement reaction is both tertiary in nature and in position is attached to a C atom  $\beta$  or  $\gamma$  with respect to the C-atom bearing the peroxy-group.

<sup>41</sup> Arndt, Barbour, Engels, Horn, and Sutton, *J.*, 1959, 3258.

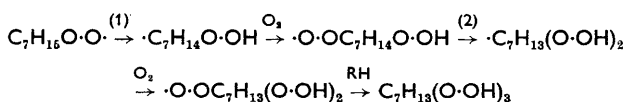
<sup>42</sup> Rust, *J. Amer. Chem. Soc.*, 1957, **79**, 4000.

<sup>43</sup> Wibaut and Strang, *Proc. Acad. Sci. Amsterdam*, 1951, **54**, B, 101, 231; 1952, **55**, B, 207.

The differences between the relative susceptibilities of transfer of H from  $\beta$ -C and from  $\gamma$ -C in monomethyl-substituted<sup>41</sup> and dimethyl-substituted<sup>42</sup> hydrocarbons are believed to be due to conformational differences introduced by the degree of chain branching. Dihydroperoxides (mainly  $\gamma$ ) have also been produced during liquid phase oxidation of n-alkanes (e.g., n-decane).<sup>44</sup>

Despite quantitative differences introduced by alteration of the precise structure of the hydrocarbon, it is established that, in general, intramolecular transfer of tertiary hydrogen is easier than that of secondary and, in turn, primary hydrogen (as expected from the relative strengths of the respective C-H bonds) and transfer of H from the  $\beta$ - and  $\gamma$ -C atoms is much more frequent than from other positions. It is noteworthy that these two modes of rearrangement involve intermediate states with 6- and 7-membered rings respectively and that scaled molecular models of  $RO_2\cdot$  radicals derived from acyclic saturated hydrocarbons show that the outer oxygen atom can approach very closely any of the hydrogen atoms on the  $\beta$ - or  $\gamma$ -C atoms.

Paper-chromatographic techniques have been developed for the separation and identification of small amounts of organic peroxides<sup>45</sup> and applied to the products of the gaseous oxidations of n-heptane, 2,2,3-trimethylbutane, n-butane, propane, and cyclohexane.<sup>46</sup> The products from n-heptane, the fuel most extensively studied, included a dihydroperoxyheptane (the positions of the OOH groups in which were not determined) and the products of its addition and condensation reactions with aldehydes. It was suggested also that an unidentified peroxidic fraction of the products, completely involatile *in vacuo* at room temperature, might contain trihydroperoxyheptane. If this is so, it is likely that its mode of formation involves *two* intramolecular rearrangements, (1) and (2):



No dihydroperoxide could be detected in the products of slow combustion of propane or of 2,2,3-trimethylbutane. In the latter case, initial attack will remove the single tertiary H; rearrangement of the resulting  $RO_2\cdot$  radical  $Me_3C\cdot CMe_2(O\cdot O\cdot)$  must therefore involve primary H. Similarly in the propane molecule, transfer from  $\beta$ -C is possible only if *both* initial attack *and* isomerisation involve primary hydrogen, and from  $\alpha$ -C only if one of these processes does. n-Butane yielded dihydroperoxybutane only under very vigorous conditions (335–345°C;  $C_4H_{10}:O_2 = 2$ ); transfer from  $\beta$ -C involves primary hydrogen once but transfer from  $\alpha$ -C involves

<sup>44</sup> Twigg, *Chem. Eng. Sci.*, 1954, 3, Suppl. 1, 5.

<sup>45</sup> Cartlidge and Tipper, *Analyt. Chim. Acta*, 1960, 22, 106.

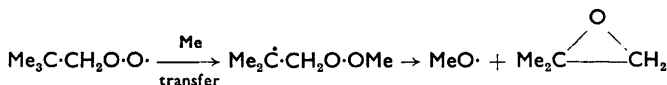
<sup>46</sup> Cartlidge and Tipper, (a) *Proc. Roy. Soc.*, 1961, A, 261, 388; (b) *Proc. Chem. Soc.*, 1959, 190; (c) *ibid.*, 1960, 219; (d) *Combustion and Flame*, 1961, 5, 87.

only sec-H. The pattern of formation of dihydroperoxides from these fuels is thus consistent with the relative ease of rearrangements involving 1,3, 1,4, 1,5, and 1,6 intramolecular H-transfer and with the strengths of primary, secondary, and tertiary C-H bonds.

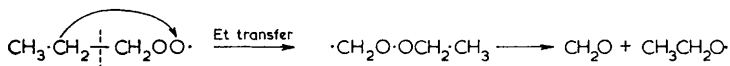
**Dicarbonyl Compounds.**—The radical  $\text{HO}\cdot\text{O}\cdot\text{C}_n\text{H}_{2n}\cdot\text{O}\cdot\text{O}\cdot$  or the dihydroperoxide  $\text{C}_n\text{H}_{2n}(\text{O}\cdot\text{OH})_2$  will decompose by homogeneous O-O fission producing carbonyl-hydroperoxides and dicarbonyl compounds. Several early ultraviolet spectroscopic studies<sup>23,47</sup> of the preflame combustion of hydrocarbons detected a strong absorption at 2600 Å, and more recent work<sup>48</sup> has established that this is due to the production of  $\beta$ -dicarbonyl compounds (e.g.,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHO}$  from  $n\text{-C}_4\text{H}_{10}$ , and  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$  from  $n\text{-C}_5\text{H}_{12}$ ) which are subsequently consumed in the cool flame. At temperatures below the cool-flame limit, the conversion of *n*-pentane into pentane-2,4-dione is as high as 10%. None of the intermediate products of *n*-butane combustion ( $\text{C}_4$  olefins, ethyl methyl ketone, crotonaldehyde, *n*-butyraldehyde, and methyl vinyl ketone) yields the  $\beta$ -dicarbonyl compound (but-3-one-1-al) on oxidation. This result strongly supports the isomerisation mechanism for its formation.

The tentative identification in the products of autoxidation of 2,6-dimethylheptane of  $\text{Me}_2\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{C}(\text{OOH})\text{Me}_2$ <sup>42</sup> suggests that trihydroperoxides decompose similarly.

**(b) Isomerisation by Group Transfer.**—Isomerisation by group transfer involves C-O bond formation and C-C fission, and subsequent decomposition by O-O fission of the isomeric radical produces an alkoxy-radical and either a carbonyl compound or an epoxide. A good example is the neopentylperoxy-radical which isomerises more readily by methyl-transfer than by hydrogen-transfer, as 1,5 intramolecular H-transfer is restricted to primary hydrogen and 1,4 intramolecular H-transfer is impossible:<sup>29</sup>



This mode of rearrangement has been successful in explaining the production of unexpected oxidation products, e.g., ethanol from propane:<sup>49</sup>



<sup>47</sup> Egerton and Pidgeon, *Proc. Roy. Soc.*, 1933, *A*, **142**, 26; Egerton and Young, *Trans. Faraday Soc.*, 1948, **44**, 750.

<sup>48</sup> Thomas and Crandall, *Ind. Eng. Chem.*, 1951, **43**, 2761; Barusch, Crandall, Payne, and Thomas, *ibid.*, p. 2764; Barusch, Neu, Payne, and Thomas, *ibid.*, p. 2766.

<sup>49</sup> Semenov, "Some Problems of Chemical Kinetics and Reactivity", Pergamon Press, London, 1958, Vol. 1, p. 99; Rezhvin, Thesis for Diploma, Moscow State University, 1951.

It has been suggested also that the isomerised radical can break down to give a smaller alkylperoxy-radical and an olefin, e.g.,<sup>28</sup>



(c) **Cyclic Hydrocarbons: Isomerisation by Ring Opening.**—Intramolecular H-abstraction in the alkylperoxy-radicals derived from hydrocarbons containing homocyclic rings is more difficult than in those derived from acyclic paraffins, because of restriction of rotation by the ring. In cyclohexane,  $\beta$ -disubstituted products have been detected, indicating that transfer of H from  $\beta$ -C occurs, but in cyclopentane this is considered unlikely.<sup>46d</sup>

An alternative mode of rearrangement of these cycloalkylperoxy-radicals is possible, however, involving the breaking of a C-C bond and the formation of an O-C bond and leads to an increase in ring size, e.g., cyclopropane:<sup>50</sup>

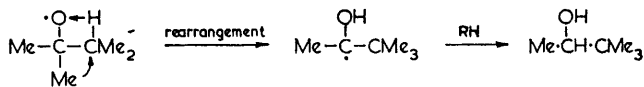


Similar mechanisms have been suggested for steps in the oxidations of cyclopentane,<sup>51</sup> methylcyclohexane,<sup>52</sup> and cyclohexene.<sup>53</sup>

### 3. Alkoxy-radical Rearrangement

Direct decomposition to a carbonyl compound and an alkyl radical is, generally, the predominant mode of reaction of alkoxy-radicals, and *intermolecular* hydrogen abstraction forming an alcohol is also of considerable importance. Rearrangement reactions, by migration to oxygen of an atom or group, have but a minor role and have not been studied as fully as the corresponding reactions of alkyl and alkylperoxy-radicals.

In the gas phase, RO $\cdot$  rearrangement involving 1,3 H-transfer and 2,1 methyl-shift has been suggested<sup>32</sup> as responsible for the formation of pinacol alcohol during the slow combustion of 2,3-dimethylbutane:



Several modes of hydrogen transfer in, and skeletal fission of, RO $\cdot$  radicals play a major part in the oxidation of esters.<sup>38,54</sup> In the "ether-oxy"

<sup>50</sup> McEwan and Tipper, *Proc. Roy. Soc.*, 1953, *A*, **216**, 280; *A*, **220**, 266.

<sup>51</sup> McGowan and Tipper, *Proc. Roy. Soc.*, 1958, *A*, **246**, 52, 64.

<sup>52</sup> Minkoff and Tipper, "Chemistry of Combustion Reactions", Butterworths, 1962, p. 166.

<sup>53</sup> Humbree, *Diss. Abs.*, 1959, **19**, 2241.

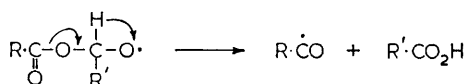
<sup>54</sup> Fish and Waris, *J.*, 1962, 4513.

radical derived from an ester by a normal "hydroperoxide" oxidation chain

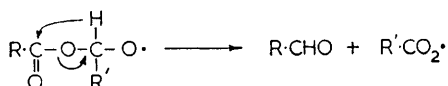


the presence of an "ethereal" linkage appears to affect the balance of competing decomposition and abstraction reactions as compared with those of unsubstituted alkoxy-radicals derived from alkanes. Thus, although direct fission to a carbonyl compound  $R'CHO$  by detachment of the largest group  $RCO_2$  (cf. ref. 34) is still of importance, abstraction of hydrogen from a further fuel molecule to give  $R \cdot CO_2 \cdot CH(OH)R'$  is negligible, no alcohol being formed. Two modes of isomerisation by H-transfer and fission of an "ethereal" C-O bond also occur:

(i) H-transfer to O

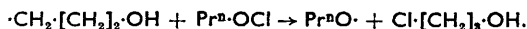
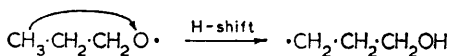


(ii) H transfer to C

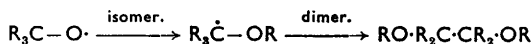


These explain qualitatively the pattern of product formation, its variation with temperature, and the effects of ester structure (*i.e.*, the identities of R and R') on the course of oxidation.<sup>38</sup>

Intramolecular hydrogen abstraction in an alkoxy-radical occurs very readily in the decomposition of hypochlorites derived from tertiary long-chain aliphatic alcohols<sup>55</sup> and from tertiary sterols,<sup>56</sup> and it has been shown recently<sup>57</sup> that the analogous reaction of primary and secondary hypochlorites will also occur and can, in several cases, lead to a free-radical chain decomposition which involves isomerisation as a necessary propagation step. For example, the thermal or photolytic conversion of n-butyl hypochlorite into tetramethylene chlorohydrin involves the linear propagation steps:



In solution, transfer to oxygen of an aryl<sup>1</sup> group



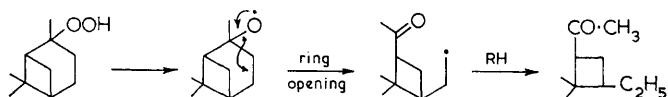
<sup>55</sup> Green, Savitz, Lau, Osterholtz, and Smith, *J. Amer. Chem. Soc.*, 1961, **83**, 2196; Walling and Padwa, *ibid.*, p. 2207.

<sup>56</sup> Akhtar and Barton, *J. Amer. Chem. Soc.*, 1961, **83**, 2213.

<sup>57</sup> Jenner, *J. Org. Chem.*, 1962, **27**, 1031.

was established as early as 1911.<sup>58</sup> More recently, the tendencies to migrate of different aryl groups have been compared;<sup>59</sup> those containing two aromatic rings (*e.g.*, *p*-biphenyl,  $\alpha$ -naphthyl) migrating six times as readily as those containing one ring only.

When R has a cyclic structure, rearrangement of RO· by ring opening may lead to interesting products. For example, during the decomposition in solution of pinane hydroperoxide, rearrangement of the pinane-oxy-radical produces an overall yield of as much as 20% of 1-acetyl-3-ethyl-2,2-dimethylcyclobutane.<sup>60</sup>

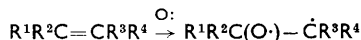


Intramolecular rearrangement of nitrogen free radicals similar to the corresponding reactions of alkoxy-radicals have been noted. Thus 1,5 H-shift propagates the decomposition of *N*-halogeno-ammonium ions,<sup>61</sup> and occurs during conversion of azides to the corresponding pyrrolidines.<sup>62</sup> It is, however, outside the scope of a Review of this length to extend the discussion to the chemistry of the isomerisation of nitrogen free radicals.

#### 4. Biradical Rearrangement

Recent work has shown that biradicals in which the two free valencies are associated with different atoms are frequently formed by addition during the oxidation of olefins, which are themselves excited into a triplet (biradical) state in the presence of oxygen.<sup>63</sup> Two cases can be distinguished, and rearrangement of the resulting biradical occurs in each.

(i) *Addition of an oxygen atom.* Addition of an oxygen atom to the double bond of an olefin is exemplified by the work of Čvetanović<sup>64</sup> on the oxidation of a range of aliphatic and alicyclic olefins by atomic oxygen which was produced by the mercury-photosensitised decomposition of nitrous oxide. The initial attack may be represented



where the  $=CR^1R^2$  group is the less highly substituted end of the double bond. The short-lived biradical produced undergoes ring closure to give an epoxide  $R^1R^2C-\underset{\text{O}}{\text{C}}R^3R^4$  (two isomers) and rearranges to carbonyl compounds:

<sup>58</sup> Wieland, *Ber.*, 1911, **44**, 3553.

<sup>59</sup> Kharasch, Poskus, Fono, and Nudenberg, *J. Org. Chem.*, 1951, **16**, 1458.

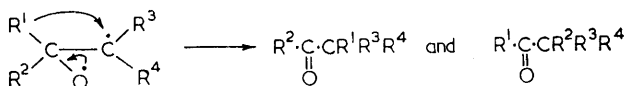
<sup>60</sup> Schmidt and Fisher, *J. Amer. Chem. Soc.*, 1954, **76**, 5426.

<sup>61</sup> Corey and Hertler, *J. Amer. Chem. Soc.*, 1960, **82**, 1657.

<sup>62</sup> Barton and Morgan, *J.*, 1962, 622.

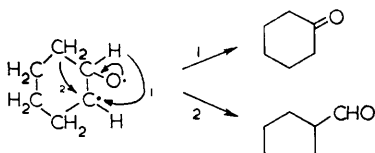
<sup>63</sup> Evans, *J.*, 1960, 1735.

<sup>64</sup> Čvetanović, *Canad. J. Chem.*, 1958, **36**, 623; Jervie and Čvetanović, *ibid.*, 1959, **37**, 529; Sato and Čvetanović, *ibid.*, p. 953; Čvetanović and Doyle, *ibid.*, 1960, **38**, 2187; Boocock and Čvetanović, *ibid.*, 1961, **39**, 2436; Jones and Čvetanović, *ibid.*, p. 2444.



Such rearrangement occurs both when  $\text{R}^1$  (or  $\text{R}^2$ ) is a hydrogen atom and when it is an alkyl group. The transfer of hydrogen atoms is entirely intramolecular; that of alkyl groups occurs by both inter- and intra-molecular mechanisms.

All these oxygenated products have, on formation, excess of vibrational energy and decompose unless deactivated by collision. From each non-aromatic olefin studied by Čvetanović, all four possible products were formed. A particularly striking example of biradical rearrangement is the production of carbonyl compounds from a cyclic olefin, which involves a reduction in ring size. With cyclohexene, for example, the two group-transfer reactions are:



and both these carbonyl compounds are indeed found in the products.

Similar biradicals derived from aromatic hydrocarbons may also rearrange in this way, but the initial products polymerise.

(ii) *Addition of an oxygen molecule.* Although the major mode of attack of most olefins by molecular oxygen is abstraction of  $\alpha$ -hydrogen to give a stabilised allyl radical, leading to  $\alpha$ -hydroperoxylation, additive attack by oxygen at the double bond appears to be important also, particularly on olefins in which the only available  $\alpha$ -hydrogen is primary<sup>65,66</sup> and on conjugated olefins.<sup>67</sup> The biradical intermediate formed,  $\text{R}^1\text{R}^2\text{C}(\text{OO}\cdot)\text{—CR}^3\text{R}^4$ , can cyclise directly to give a four-membered cyclic peroxide,<sup>65,66</sup> or (if derived from a diene) *via* a resonant form to give a six-membered cyclic peroxide,<sup>67c</sup> or by true rearrangement. A full study of this last case has involved the use of <sup>14</sup>C-tracer techniques to determine the pattern of product formation during the slow combustion of 2-methylbut-2-ene.<sup>66,68</sup> In this case, the biradical produced by addition of oxygen to the less-substituted end of the double bond is  $\text{Me}_2\text{C}\text{—C}(\text{OO}\cdot)\text{HMe}$ , cyclisation of which gives an unstable four-membered cyclic peroxide which decomposes rapidly producing equimolar amounts of acetone and acetaldehyde, the major products. Minor oxidation products include, however,

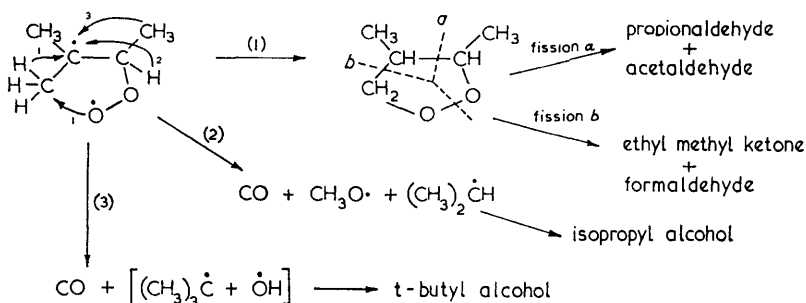
<sup>65</sup> Dobrinskaya and Neiman, *Doklady Akad. Nauk S.S.S.R.*, 1947, **58**, 1919.

<sup>66</sup> Cullis, Fish, and Turner, *Proc. Roy. Soc.*, 1961, *A*, **262**, 318; 1962, *A*, **267**, 433.

<sup>67</sup> (a) Bergmann and McLean, *Chem. Rev.*, 1941, **28**, 367; (b) Dufraisse, *Bull. Soc. chim. France*, 1939, **6**, 422; (c) Farmer, *Trans. Faraday Soc.*, 1946, **42**, 228.

<sup>68</sup> Cullis, Fish, and Trimm, "Ninth Symposium on Combustion", Academic Press, New York, 1963, p. 167.

ethyl methyl ketone, propionaldehyde, formaldehyde, isopropyl alcohol, and *t*-butyl alcohol. Isotopic labelling of the 2- and the 4-carbon atom in turn has established that the modes of formation of these compounds are consistent with the following isomerisations of the biradical:



- (1) H-Transfer and ring closure  
 (2) H-Transfer and decomposition  
 (3) Me Transfer and decomposition

The formation of *t*-butyl alcohol, in which the 4-C atom of the original olefin has become linked directly to the 2-C of the olefin, is particularly strong evidence of rearrangement.

## 5. Applications

(a) **Preparative Applications.**—The production of useful chemicals by gaseous oxidation of hydrocarbons is an economically attractive route as the materials and processing are cheap compared with those associated with most types of reaction. Alkylperoxy-radical rearrangement reactions produce useful chemicals such as *O*-heterocycles and carbonyl compounds and it is not surprising that attempts have been made to maximise the yields of these. One of the most successful of these<sup>30</sup> used a reaction vessel consisting of a continuous cycling system in which inert solid particles of *ca.* 300 $\mu$  diameter constantly rained down through the reaction zone, removing the heat produced by the homogeneous gas-phase reaction. Further oxidation of the useful products initially formed by rearrangement is thus prevented. The proportion of solids needed to achieve the desired control of temperature was low enough to eliminate surface effects, the reaction mechanism being essentially the same as in an open tube. Such a reaction system has been used for oxidising, under oxygen-deficient conditions, a wide range of hydrocarbons from ethane to petrolatum wax, over a large temperature range (300°–650°C). In many cases (*n*-hexane, *n*-heptane, *n*-decane, *n*-hexadecane, cyclohexane, methylcyclohexane, and methylcyclopentane) the total yields of epoxides were considerable (25–55% by weight of the hydrocarbon feed), particularly at low temperatures. The epoxide fractions from *n*-alkane oxidation contained



quite complex mixtures of individual epoxides (see page 254), the major components of which were those epoxides formed by initial attack at the 2-C atom followed by transfer of H from  $\beta$ - and from  $\gamma$ -C in the alkylperoxy-radical. The mixture from n-hexane, for example, contained 47% of 2,5-dimethyltetrahydrofuran and 30% of 2-ethyl-4-methyloxetan, and from n-heptane 57% of 2-ethyl-tetrahydro-5-methylfuran and 26% of 4-methyl-2-n-propyloxetan. In the oxidation of branched-chain and cyclic hydrocarbons, initial abstraction of tertiary hydrogen occurred most frequently, the mode of rearrangement of the resulting alkylperoxy-radicals being determined sterically. Thus 2,2,4-trimethylpentane produces predominantly tetrahydro-2,2,4,4-tetramethylfuran, 2,4-dimethylpentane gives tetrahydro-2,2,4-trimethylfuran, and methylcyclohexane gives 1,2-epoxy-1-methylcyclohexane. In general, higher pressures are necessary in order to obtain considerable yields of epoxides from branched alkanes than from n-alkanes.

These experiments were carried out using hydrocarbons on the gallon scale and indicate that the production of useful oxygenated chemicals by carefully controlled gaseous oxidation may soon become economically viable.

(b) **Kinetic Applications.**—(i) *The rate-temperature dependence of oxidation.* One of the most striking features of the gaseous oxidation of hydrocarbons and their derivatives is the complicated dependence of the rate on temperature. Rate-temperature curves for the slow combustion of a wide range of fuels show marked regions of "negative temperature coefficient", and this phenomenon of decrease in rate with increase of temperature is reflected also in the ignition curves of the fuels. Indeed, plots of ignition temperature against pressure for given mixtures with air of a hydrocarbon show not only a low-temperature region (associated with the occurrence of cool flames leading to two-stage ignition) and a high-temperature region, but the former exhibits also "fine structure". The low-temperature regions for n-alkanes such as n-hexane,<sup>69</sup> n-heptane,<sup>70</sup> and n-octane<sup>70</sup> consist of three lobes; certain of these are absent for hydrocarbons with branched chains or cyclic structures and for n-alkanes of low molecular weight. For example, if the n-heptane lobes be designated L1, L2, and L3, in order of increasing temperature, the low-temperature ignition of 2,2,4-trimethylpentane<sup>70</sup> shows lobes corresponding to L2 and L3, of cyclohexane<sup>69</sup> to L1 and L2, and of ethane to L3,<sup>71</sup> while methane<sup>71</sup> is unique among the alkanes in possessing no low-temperature ignition region.

In order to explain the phenomenon of negative temperature coefficient it is necessary to postulate that, as temperature increases, the predominant mode of oxidation changes from a branching process to a non-branching

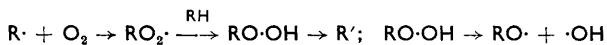
<sup>69</sup> Burgoyne, Tang, and Newitt, *Proc. Roy. Soc., A*, **174**, 379.

<sup>70</sup> Maccormac and Townend, *J.*, 1938, 238.

<sup>71</sup> Kane, Chamberlain, and Townend, *Proc. Roy. Soc., A*, **160**, 174.

process, and subsequently a further branching process occurs, causing the rate to increase again. In cases where a low-temperature ignition diagram contains several lobes (due to repeated fluctuations of the net branching factor,  $\phi$ , as temperature rises, cool flames being formed when  $\phi$  is sufficiently large), such a sequence of events must be repeated several times as temperature is increased.

One of the most successful attempts to account for these rate-temperature phenomena, the associated production of cool flames and the marked dependence of the "fine structure" of low temperature ignition on molecular structure, has described them in terms of the isomerisation reactions of alkylperoxy-radicals. It is well-known that, in slow combustion at low temperatures, degenerate branching may result from the breakdown (producing two radicals) of monohydroperoxides RO·OH which are formed by a linear chain involving *intermolecular* H-abstraction by RO<sub>2</sub>·:



As the temperature is increased *intramolecular* hydrogen abstraction (which is unimolecular but has a high activation energy) will become more important, competing with formation of hydroperoxide. Unimolecular decomposition of the rearranged radical [to a cyclic ether and a hydroxyl radical (p. 253)] will provide a non-branching process (producing only one radical) and reduce the rate,<sup>26</sup> whereas other modes of reaction such as further oxidative attack giving C<sub>n</sub>H<sub>2n</sub>(O·OH)<sub>2</sub> (p. 258) and breakdown of this compound produce more than one radical and thus provide a branching process, increasing the rate again.<sup>46d</sup> Moreover, several modes of RO<sub>2</sub>· isomerisation (by transfer of primary, secondary, or tertiary hydrogen from the  $\alpha$ ,  $\beta$ ,  $\gamma$ , or  $\delta$ -carbon atom) are possible and the activation energies of these will differ, increasing with increasing C-H bond strength and with decreasing transition-state ring size. The setting up of *several* branching-non-branching competitions, resulting in several lobes on an ignition curve, is thus explicable.<sup>72</sup> Further, the number and ease of such possible modes of rearrangement is a function of molecular structure and explains well the differences in the ignition curves of various hydrocarbons. For example, the L1 zone is considered to involve isomerisation by transfer of secondary or tertiary hydrogen from  $\beta$ - or more distant C atoms, and is therefore absent in cases such as ethane or 2,2,4-trimethylpentane the alkylperoxy-radicals from which do not have such hydrogen available. Similarly the L2 zone may be formed by transfer of secondary hydrogen from an  $\alpha$ -C atom and the L3 zone by transfer of primary hydrogen.

(ii) *The knock ratings of fuels.* It is well established that most fuels "knock" by the low-temperature process of ignition<sup>73</sup> and that the knock

<sup>72</sup> Walsh, "Ninth Symposium on Combustion", Academic Press, New York, 1963, p. 1046.

<sup>73</sup> Downs, Walsh, and Wheeler, *Phil. Trans.*, 1951, **243**, 463.

resistance of a fuel is correlated with its resistance to cool-flame formation.<sup>74</sup> The dependence of these ignition processes on isomerisation reactions of alkylperoxy-radicals, as described in the preceding section, offers an understanding of why knock ratings are such a sensitive function of molecular structure and explains in principle the relative knock ratings of fuels in terms of the chemical reaction steps which lead to knock. It has long been realised that, in order to explain knock ratings, it is necessary to postulate that remote groups can affect what is happening at the site of the free valency<sup>21b</sup> and it is difficult to see how this can occur other than by an isomerisation reaction. More recently, the relation of tendency to knock to tendency to form dihydroperoxides by  $RO_2\cdot$  isomerisation and further oxidation to  $HO\cdot O\cdot C_nH_{2n}\cdot O\cdot O\cdot$  has been pointed out for a wide range of fuels<sup>46d</sup> and the relation between knock rating, low-temperature ignition diagram, and molecular structure has been discussed fully by Walsh<sup>72</sup> in terms of the number and ease of possible modes of rearrangement of the alkylperoxy-radicals derived from hydrocarbon fuels.

<sup>74</sup> Barusch and Payne, *Ind. Eng. Chem.*, 1951, **43**, 2329.