781. *Slow Oxidation of Hydrocarbons in the Gas Phase. Part I. Reactions during the Induction Period of Isobutane Oxidation.*

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The slow oxidation of isobutane in a static system at about 300° has been investigated with special reference to the chemical changes which occur during the induction period. Analysis by means of gas-liquid chromatography with sensitive detectors showed that the concentrations of many primary products (isobutene, isobutene oxide, propionaldehyde, acetone, methanol, propene, propene oxide, acetaldehyde, etc.) increase according to a relation $C = C_0e^{\phi t}$. For nearly all products the branching factor ϕ was found to have about the same value. The reactions during the induction period, which are less complex than those in later stages, have been formulated as a degenerate chain-branching mechanism involving chain-propagating reactions of both isobutyl and t-butyl radicals. During the induction period the products are formed by intramolecular decomposition of the butylperoxy-radicals.

Slow oxidation of hydrocarbons is often characterized by an induction period during which the conversion is very small. The reactions during this stage are of great importance since they lead ultimately to the oxidation process proper. The whole process is usually described by a degenerate chain-branching mechanism, and in particular the nature of the intermediate responsible for branching has been discussed extensively. Although the branching reactions determine the overall kinetics of the oxidation the formation of the products will be due to the straight-chain reactions. Investigations of mixture composition with increasing conversion, as measured by the pressure rise, seem to indicate that different mechanisms operate during and after the induction period.[1] A similar conclusion was reached by Knox [2] who studied the formation of gaseous products in the slow oxidation of propane in relation to the pressure rise.

Unfortunately not many details of reactions occurring in the induction period are available since the product concentrations during this period are very low. Hitherto, therefore, most of the conclusions have been drawn, not from chemical analyses, but from the effect of additives on the length of the period. The recent development of very sensitive detectors for gas-chromatographic analyses makes these low concentrations no longer inaccessible to investigation. This has enabled us to study the elementary reactions in the oxidation of isobutane by following the concentrations of the products, especially during the induction period. Since secondary reactions do not yet occur, the products here arise only from the substrate and not from an ill-defined reaction mixture. The information on the elementary reactions was derived from three sources: the peculiarities

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[1] Batten, Gardner, and Ridge, *J.*, 1955, 3029.

[2] Knox, *Trans. Faraday Soc.*, 1960, **56**, 1225.

of the concentration–time curves, the identities of the products and their relative abundance, and the ratio between the concentrations of various products under different conditions.

EXPERIMENTAL

Mixtures of pure isobutane and oxygen were introduced rapidly into a static reaction system up to a pre-determined pressure. The reaction was followed by determining the pressure continuously with a recording differential manometer of the spoon type.[3] After the reaction vessel had been aged in order to give reproducible results the oxidation was studied under a variety of conditions (pressure 100—400 mm. Hg; temperature 260—360°; isobutane : oxygen 9 : 1 to 1 : 4). Usually only those reactions were followed which had induction periods between 2 and 120 min. Concentration–time curves were determined for several oxidation products from the smallest measurable conversion up to complete reaction by interrupting successive experiments after increasing times or after increasing pressure changes. The reactions are quite reproducible but it proved necessary to relate reactions with large conversions by means of a standard pressure–time curve instead of relying exclusively on the reaction time.

For the analysis a large fraction of the reactants was transferred to the sampling tube of the gas–liquid chromatography system. Samples were kept in the gaseous state throughout in order to avoid liquid-phase reactions such as the addition of peroxides to aldehydes. The first chromatographic column (stationary phase: polyethylene glycol, average mol. wt. 400) effects a separation of the high-boiling oxygenated products and the rapidly eluted mixture of hydrocarbons, carbon oxides, and oxygen is separated on the next column (stationary phase: dimethylsulpholane). The application of flame ionization as well as katharometer detection and the use of relatively large samples enabled us to detect many compounds, even during early stages of the induction period.

The main intermediates observed were, in order of relative abundance: isobutene, acetone, isobutene oxide, propionaldehyde, acetaldehyde, methanol, propene, propene oxide, carbon dioxide, isobutyraldehyde, 3-methyloxetane, and methacraldehyde. The identity of the products was checked by determination of one or more of the following properties: (1) Retention volume on various columns. (2) Variation of the retention volume with temperature. (3) Mass-spectrum (of a frozen-out compound). (4) Infra-red spectrum (of a frozen-out compound). (5) Ratio of the signals of two essentially different detectors placed at the end of the same column. This ratio does not depend on the amount eluted or on the column used but only on the properties of the eluted molecule (and sometimes the carrier gas) and on the methods of detection.

A preliminary identification of various types of compound was effected by insertion of special absorption columns into the gas–liquid chromatographic system, *e.g.*, mercuric nitrate on ethylene glycol for selective removal of olefins. Hydrogen peroxide was detected by the test with titanium sulphate performed on the collected material of many interrupted reactions, but no results are available on its concentration and that of water, since these products could not be determined by our chromatographic methods.

RESULTS AND DISCUSSION

Fig. 1 shows the dependence of the logarithm of concentration (log C) on time for the various products formed in the oxidation of isobutane. The results are presented in this manner since an exponential relation is to be expected according to the theory of degenerate chain branching.[4] It is seen that three stages can be clearly discerned in the oxidation. The third stage corresponds with the usually investigated oxidation from the end of the induction period onwards. The second stage covers most of the induction period and is characterized by the linear dependence of the log C on time, the concentration of some of the products increasing a hundred-fold in this period. Owing to the very low concentrations involved the first pre-exponential stage is only observed for isobutene but it must always be present since log C will tend to minus infinity for t approaching zero.

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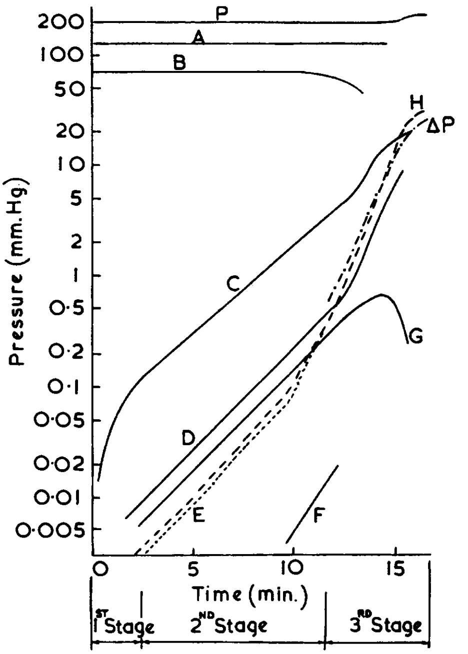
[3] Sterk, unpublished work.

[4] Semenov, " Some Problems of Chemical Kinetics and Reactivity," Pergamon Press, London, 1958.

In the second stage the formation of isobutene is accompanied by that of acetone, isobutene oxide, propionaldehyde, isobutyraldehyde, propene, acetaldehyde, propene oxide, and methanol, while in the third stage additional small amounts of ethylene, ethane, 3-methyloxetane and methacraldehyde can be detected. Carbon dioxide is one of the main products in this stage.

The exponential concentration rise observed during the second stage confirms a mechanism of degenerate chain branching. Since the products in this stage show approximately equal net chain-branching factors ϕ_i [given by the value of $(d \ln C_i/dt)$ in the middle of the induction period], *i.e.*, constant concentration ratios, they are formed in parallel reactions. Only for isobutene is the branching factor somewhat smaller, which may be the result of secondary oxidation. The net branching factors vary qualitatively in the usual way, *i.e.*, ϕ rises with increasing temperature, total pressure, or hydrocarbon : oxygen ratio. Since any degenerate chain-branching reaction will result in an exponential dependence it is questionable whether many details on the mechanism can be derived from this relation.



Dependence, on time, of pressure of reactants and intermediates in the oxidation of isobutane at 300°.

P = *Pressure.* A = *Isobutane*; B = *oxygen*; C = *isobutene*; D = *isobutene oxide*; E = *propene*; F = *propene oxide*; G = *propionaldehyde*; H = *acetone and methanol.*

Deviations from the exponential increase begin at the end of the induction period (the beginning of the third stage). Some curves, *e.g.*, those for acetone and isobutene oxide, continue at a steeper slope while the concentration of isobutene, for example, tends to become stationary. The curves for acetaldehyde and propionaldehyde even pass through a marked maximum. At this stage carbon dioxide becomes important and its exponential rise roughly parallels the steeper part of the acetone and isobutene oxide curves. The curve giving the pressure rise in this stage as a function of time is parallel to the corresponding parts of the concentration curves mentioned. In many cases the slope of this part of the lines is about twice the slope of the concentration curves during the induction period. This may be explained as follows:

At the end of the induction period the concentration I of products, which increases according to the relation $I = I_0 . e^{\phi t}$, becomes so great that interaction with radicals becomes comparable with the reaction of the starting material. Hence the concentration P of products of this interaction is found from $dP/dt = kIR$. Since the concentration R of the attacking radicals also increases exponentially ($R = R_0e^{\phi t}$) the branching factor of the products P is twice that of the products I. This situation is met with for acetone and isobutene oxide. Some products (*e.g.*, carbon dioxide) formed in secondary reactions will appear only at this stage and consequently their concentrations rise immediately with a branching factor 2ϕ.

Simultaneous consumption and formation of products may result in a constant concentration (isobutene) or even decrease (propionaldehyde).

The pressure rise also fits into this picture. During the initial stages of the reaction the chain-propagation usually involves breaking of one bond of the stable molecule with formation of another bond, *e.g.*, $HO\cdot + RH \longrightarrow H_2O + R\cdot$. These reactions proceed with small ΔH and do not increase the number of molecules. In later stages reactions between intermediate products and radicals occur which involve weaker bonds, *e.g.*, $HO\cdot + R\cdot CHO \longrightarrow H_2O + CO + R\cdot$. The change in free enthalpy can now become sufficient for subsequent dissociation of one of the products to become possible. The pressure rise must be due to such processes and a 2ϕ-dependence is therefore to be expected.

Other important features of the second stage of the induction period are: the occurrence of hydrogen peroxide; and the large concentration of isobutene, relatively not only to that of the other products, but also to the pressure rise which in this stage is much smaller than the increase in isobutene concentration. The preferential formation of isobutene as a primary product stands in contrast to the usual notion that dehydrogenation is the normal process at high temperature (about 500°) while the formation of oxygenated products is favoured by a low temperature. The facts mentioned suggest that the main overall process, which involves no pressure change, is:

$$CHMe_3 + O_2 \longrightarrow CH_2{:}CMe_2 + H_2O_2$$

This reaction may be composed of the following elementary steps:

$$i(t)\text{-}C_4H_9\cdot + O_2 \longrightarrow CH_2{:}CMe_2 + HO_2\cdot$$
$$HO_2\cdot + CHMe_3 \longrightarrow i(t)\text{-}C_4H_9\cdot + H_2O_2$$

The low concentration of the intermediates during the second stage of the induction period makes reactions between non-radical intermediates and oxygen negligible. All the products will therefore arise in parallel reactions starting from butyl radicals, both primary (iso) and tertiary. These radicals will react rapidly with oxygen to yield the butylperoxy-radicals, which are thought to give the products by internal rearrangement followed or accompanied by decomposition. The rearrangement involves either breaking of a C–H bond with formation of an O–H bond[5] or breaking of a C–C bond with formation of a C–O bond,[6] which is thermodynamically more favourable. Intramolecular decomposition will be favoured over intermolecular abstraction by the molecular conformation and the relatively long intervals between collisions in low-pressure gas-phase reactions. By this formulation a straight-forward explanation for the formation of *all* products can be given. When, in addition, a small fraction of the butylperoxy-radicals abstract hydrogen atoms intermolecularly, this would explain the observed slow chain branching. A mechanism[7] involving butyl hydroperoxide as key intermediate cannot explain the formation of all products and the slowness of the branching.

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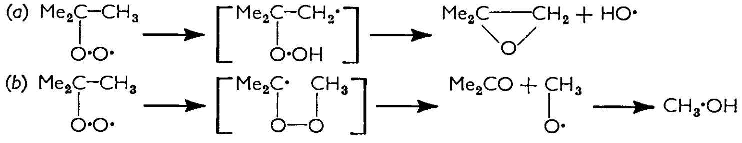
[5] Walsh, *Trans. Faraday Soc.*, 1947, **43**, 297.

[6] Shtern and Chernyak, *Doklady Akad. Nauk S.S.S.R.*, 1951, **78**, 91; Bailey and Norrish, *Proc. Roy. Soc.*, 1952, *A*, **212**, 311.

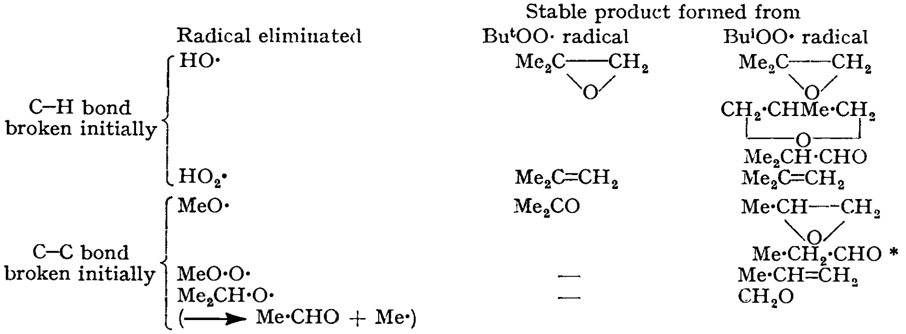
[7] Bose, *Trans. Faraday Soc.*, 1959, **55**, 778.

Examples of possible reactions for the oxidation of isobutane are:



All possibilities for intramolecular decomposition of butylperoxy-radicals have been summarized in Table 1 and all these products have indeed been observed.

TABLE 1. *Decomposition reactions of butylperoxy-radicals.*



	Radical eliminated	Stable product formed from Bu^{t}OO· radical	Stable product formed from Bu^{i}OO· radical
C–H bond broken initially	HO·	Me_2C——CH_2 \O/	Me_2C——CH_2 \O/ CH_2·CHMe·CH_2 (—O—) Me_2CH·CHO
	HO_2·	$Me_2C{=}CH_2$	$Me_2C{=}CH_2$
C–C bond broken initially	MeO·	Me_2CO	Me·CH—CH_2 \O/ Me·CH_2·CHO *
	MeO·O·	—	Me·CH=CH_2
	Me_2CH·O· (⟶ Me·CHO + Me·)	—	CH_2O

* By rearrangement of the intermediate radical.

In a few cases even the relative abundance or scarcity of products can be understood. Thus molecular models indicate that the free valency on the oxygen atom of the $Me_2CH{\cdot}CH_2{\cdot}O{\cdot}O{\cdot}$ radical will be further removed from the hydrogen atoms of the CH_2 group than from the hydrogen of the CH group; if differences in C–H bond strength are neglected, the reactions leading to isobutyraldehyde may be expected to be slower than that leading to isobutene oxide. This is in accordance with the concentrations found. The low yield of 3-methyloxetane may be due to the much greater C–H bond strength in the methyl groups. Since this effect becomes smaller at higher temperature it is understandable why Jones and his co-workers found larger concentrations in their experiments. The experimental fact that isobutyraldehyde attains large concentrations in mixtures that have fully reacted can be explained by the subsequent thermal isomerization of isobutene oxide to isobutyraldehyde which has been checked in separate experiments. Only the formation of methacraldehyde, observed in the later stages of the induction period, does not fit directly into our scheme. We found, however, that this compound is formed readily from the main primary product, isobutene.

Variation of the total pressure, temperature, or composition has remarkably little influence on the relative abundance of the various products. Only the increase in ratio of both acetaldehyde and propionaldehyde to, *e.g.*, acetone as oxygen-content increases is very striking. It may well be connected with the different precursors of acetone and the aldehydes, *viz.*, t-butyl and isobutyl radicals, respectively. A tentative explanation would be the following:

Isobutyl and t-butyl radicals are formed by hydrogen abstraction from isobutane. The difference in activation energy for the H-abstraction by, *e.g.*, ·OH from the primary and the tertiary carbon atom in isobutane is unknown. Knox and Trotman-Dickenson [9]

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[8] Jones, Allendorf, Hutton, and Fenske, Preprints Amer. Chem. Soc. Meeting, 1959, **4**, C–17.

[9] Knox and Trotman-Dickenson, *Chem. Soc. Special Publ.*, 1957, No. **9**, p. 41.

have, however, investigated the comparable abstraction by Cl-atoms and found a value of 340 cal./mole for the difference in activation energy of the processes:

$$Cl + Me_3CH \longrightarrow HCl + Me_2CH{\cdot}CH_2{\cdot}$$
$$Cl + Me_3CH \longrightarrow HCl + Me_3C{\cdot}$$

If a similar low value is accepted for the abstraction by •OH, this will not be sufficient to offset the statistical advantage of isobutyl radicals. Both butyl radicals react with oxygen to give butylperoxy-radicals, which finally give the stable products. In addition the following reaction may occur:

$$Me_2CH{\cdot}CH_2{\cdot} + Me_3CH \longrightarrow Me_3CH + Me_3C{\cdot}$$

since t-butyl is thermodynamically more stable than isobutyl radicals. In mixtures with a high concentration of isobutane most products will therefore be formed from t-butylperoxy-radicals, whereas high oxygen concentrations will cause the isobutyl radicals to react immediately with oxygen and therefore result in high aldehyde concentrations.

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