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PEROXIDES IN THE COMBUSTION OF ISOBUTANE¹

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ABSTRACT

A survey has been made of the nature of the peroxides occurring in the combustion of isobutane below and above the lower cool-flame limit. The peroxides were resolved and partially identified by paper chromatography. Below the cool-flame limit, the peroxide is found to be mostly *tert*-butyl hydroperoxide, with some hydrogen peroxide, but as the cool-flame limit is approached the proportion of *tert*-butyl hydroperoxide declines, while that of hydrogen peroxide increases. In addition, peroxides identified as aldehyde and acid peroxides increase as the cool-flame limit is approached. No *tert*-butyl hydroperoxide appears to survive the cool flame, although copious quantities of aldehyde peroxide and hydrogen peroxide remain.

INTRODUCTION

The nature and role of the peroxides occurring in the products of the non-catalyzed thermal oxidation of hydrocarbons has been the subject of considerable debate, and the problem has been complicated by the absence of a reliable analytical technique, capable of identifying peroxides in the amounts usually prevailing in the study of combustion reactions. The possible occurrence of various types of peroxides in combustion reactions has recently been considered by Tipper (1). While several unequivocal identifications have been claimed, these are for the most part confined to exceptional cases, for example the low-temperature combustion of acetaldehyde (2).

A paper chromatographic method of resolving some peroxide mixtures has recently been briefly described, and applied in the analysis of the cool-flame combustion products of ethyl benzene (3). The application of this technique has now been extended over a further range of peroxides and its use in the analysis of the combustion products of isobutane is the subject of the present paper.

Isobutane is a rather exceptional fuel, in that it possesses nine primary hydrogen atoms and only one tertiary hydrogen atom. That this latter atom is the initial point of attack by oxygen has been demonstrated by Batten, Gardner, and Ridge (4). Further, the hydroperoxide derived from isobutane, *tert*-butyl hydroperoxide, is unique among the lower alkyl hydroperoxides in its thermal stability. From the point of view of the possible identification of alkyl hydroperoxide in a hydrocarbon oxidation product, the combustion of isobutane thus appears particularly attractive. Batten, Gardner, and Ridge analyzed their combustion products in some detail and, apart from the inevitable gaseous product, found formaldehyde, a smaller amount of higher aldehyde, acetone, a little acid, and peroxides. The peroxides were further examined by polarography with successive removal of various components. Hydrogen peroxide was removed by reaction with

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titanous chloride and ammonia. Formaldehyde peroxide (and, the authors conclude, higher aldehyde peroxide also) was removed by reaction with mercury. The residual peroxide was assumed on the basis of its polarogram to be alkyl hydroperoxide. From this procedure, the authors concluded that alkyl hydroperoxide, probably *tert*-butyl hydroperoxide, could form more than 50% of the total peroxide.

An examination of their polarograms immediately reveals that the identification of the peroxide is by no means unequivocal, as the authors themselves make clear. Nevertheless, the occurrence of *tert*-butyl hydroperoxide and hydrogen peroxide appeared highly probable, the former compound especially in the induction period.

The present work entirely confirms the conclusions of Batten, Gardner, and Ridge by providing identifications which can be open to very little uncertainty.

EXPERIMENTAL

Isobutane, a gift from the British Petroleum Company Limited, contained 0.5%*n*-butane as the sole detectable impurity. Oxygen was obtained from a cylinder and was used without further treatment.

The reaction was studied using a flow system similar to that already described (3). The reaction vessel was a pyrex cone, 15 cm long, 2.5 cm maximum diameter. The fuel to oxygen ratio was 1 to 1, total pressure atmospheric. The products were passed through a trap at -80° C. At the end of a run the trap was allowed to warm up, isobutane evaporating off. The residual liquid was used in the identification of peroxides. Drops of liquid were paper chromatographed as previously described. The solvent system used was butanol-ether-water (10:10:1). The chromatograms were developed with aqueous acidified potassium iodide solution. The unknown chromatograms were compared with those of standards run on the same paper.

The standard peroxides, whose R_F values are shown in Table I, were: methoxy hydroperoxide and dimethoxyperoxide (formaldehyde peroxides); α -hydroxyethyl hydroperoxide and α, α' -dihydroxydiethyl peroxide (acetaldehyde peroxides); *tert*-butyl hydroperoxide, and hydrogen peroxide. Aldehyde peroxide was made by desiccating an aqueous mixture of aldehyde and hydrogen peroxide containing a drop of sulphuric acid, over concentrated sulphuric acid. The end product of the formaldehyde mixture was a mildly explosive, insoluble solid, shown by Rieche and Meister (5) to be tetraoxymethylene diperoxide. This contained a little material soluble in water, which was dimethoxyperoxide. A compound which was almost certainly methoxy hydroperoxide was obtained only as an intermediate in the initial stage of the reaction. A similar sequence occurred in the acetaldehyde reaction, but here polymer was not obtained. The end product was a hygroscopic, very explosive oil. In addition, butyraldehyde and caproaldehyde were shaken with hydrogen peroxide; some reaction occurred producing compounds of R_F value 0.99–1.0. In general, pure peroxides were not isolated, aqueous solutions being adequate for the present purpose.

RESULTS

The oxidation of isobutane was studied at 250, 330, 360, and 370° C. A cool flame appeared at about 350° C.

(a) At 250° C, total flow 0.4 ml per sec, run time 195 minutes.—A trace of aqueous product, strongly peroxidic, remained in the trap. The R_F values of the peroxides were 0.99 and 0.50. A smudge, of maximum density at 0.85, also was formed. The component of R_F 0.99 strongly predominated.

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(b) At 330° C, total flow 2.0 ml per sec, run time 30 minutes.—The product was similar to the above. The proportion of material of R_F 0.99 was somewhat decreased, while that of R_F 0.50 increased. The smudge was also denser.

(c) At 360° C, total flow 2.0 ml per sec, run time 15 minutes. Weak cool flame.—The degree of oxidation was considerably increased, and an appreciable volume of liquid product was formed. The R_F values of the peroxides were 0.50 and 0.9; the latter spot was actually a streak, extending between 0.95 and 0.7. The component of R_F 0.99 was almost certainly absent.

(d) At 370° C, total flow 2.0 ml per sec, run time 30 minutes. Bright cool flame.—The product was treated as in (c). No component of R_F 0.99 was present, although the density of the 0.7–0.95 smudge was considerably increased. The component of R_F 0.50 was also present.

DISCUSSION

A comparison of the R_F values of the unknown peroxides with the R_F values of the standards shows that the unknown peroxide of R_F 0.50 is almost certainly hydrogen peroxide. It is interesting that this compound is a product of the low-temperature reaction, as it has generally been assumed to be characteristic more of a high-temperature reaction. The possibility that the hydrogen peroxide detected is actually a result of decomposition of organic peroxide during the analysis is ruled out by the fact that spots, not streaks, were obtained in the chromatography of the standards.

The spot of $R_F 0.99$ exactly matches that of *tert*-butyl hydroperoxide. The identification of this component as *tert*-butyl hydroperoxide is strongly substantiated by the conditions of its appearance. It is a product of the induction period, that is, a primary product, and disappears as the degree of reaction increases, that is, as the cool-flame limit is crossed. This behavior is exactly the reverse of that of aldehydes—and hence, aldehyde peroxides—which are the predominant products of cool-flame reactions (e.g. propane (6) and hexane (7)). It is improbable, therefore, that the fast-moving peroxide is a higher aldehyde peroxide possibly derived from the preferential combustion of the trace of *n*-butane in the starting material.

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The material of R_F 0.7–0.95 was a minor component below the cool-flame limit, but increased markedly as the limit was crossed. A comparative study of the cool-flame oxidation of a wide variety of hydrocarbons and ethers showed that this material is a characteristic product of all the oxidations. A comparison of its chromatographic behavior with that of the standards suggests that its composition is complex, and it is believed that the material is a mixture of aldehyde and acid peroxides not completely resolved. The presence of alkyl hydroperoxides is not ruled out, but the conditions of its occurrence would appear to preclude the presence of alkyl hydroperoxides.

TABLE I	
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R_F values of standard peroxides

Peroxide	R_F
Hydrogen peroxide Methoxyhydroperoxide Dimethoxyperoxide α-Hydroxyethyl hydroperoxide α,α'-Dihydroxydiethyl peroxide tert-Butyl hydroperoxide	$\begin{array}{c} 0.50 \\ 0.65 \\ 0.82 \\ 0.73 \\ 0.95 \\ 0.99 \end{array}$

Solvent: n-Butanol-ether-water (10:10:1 v/v). Paper: Whatman No. 3. Developer: Acidified potassium iodide.

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It is concluded, therefore, that in the oxidation of isobutane, the peroxide products are hydrogen peroxide, tert-butyl hydroperoxide, and aldehyde peroxides. Tert-butyl hydroperoxide is the predominant product of the induction period, along with some hydrogen peroxide. As the cool-flame limit is passed, the yield of *tert*-butyl hydroperoxide suffers a catastrophic decline while the yields of aldehyde peroxides and hydrogen peroxide increase.

This behavior appears to substantiate the conclusions of Batten, Gardner, and Ridge. The decline in their total peroxide after the induction period was ended (in contrast with the present data) is probably a result of consumption of reactant in their static apparatus.

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