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EXPLOSION REACTION OF OLEFINS

III Explosion Reaction of *trans*-Butene—2-Oxygen Mixtures

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The explosion reaction of *trans*-butene-2 (T2B) has been examined by means of gas chromatography under the following conditions: temperatures, 480°C and 430°C, composition, 40 and 50 vol % of T2B, respectively. Emphasis is placed on the detection of the intermediates of this reaction.

It is found that the major intermediate of the explosion reaction is acetaldehyde and is identical with that of the slow combustion. It is confirmed that acetaldehyde is the intermediate of the reaction caused in the low temperature peninsula and plays a role in the isochor curves of type III. The production of acetaldehyde can be accounted for by considering that oxygen initially adds across the double bond in order to form cycloperoxide which decomposes subsequently.

Introduction

It has long been known that hydrocarbons can react with oxygen in several ways, and it has been convenient to divide the combustion processes into four categories[1]: (1) slow reaction, (2) coolflames, (3) two-stage ignition and (4) one-stage or hot ignition. The slow combustion of butene-2 at low temperatures below about 400°C has been studied by a few workers[2~4]. Porter[3] *et al.* and Tse[4] have attempted at a detailed study the reaction during the induction period, and have found that acetaldehyde is the major intermediate and degenerate branching agent, and that no difference in behavior of the *cis* and *trans* forms can be detected. Neuman *et al.*[5] and Ray *et al.*[6] have also studied the reaction taking place during the coolflame induction period, and have found that acetaldehyde is the major product. Ray *et al.*[6] have showed that considerable amount of 2, 3-epoxybutane is produced after the passage of the coolflame.

Little information is available concerning the reaction taking place at high temperatures above about 400°C and in the hot ignition (explosion) region. Two groups[7,8] have studied the reaction at

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1) J. A. Barnard and A. Watts, *Combust. Sci. Tech.*, **6**, 125 (1972)
2) A. Blundell and G. Skirrow, *Proc. Roy. Soc.*, (London), **A244**, 331 (1958)
3) R. G. W. Norrish and K. Porter, *ibid.*, **A272**, 164 (1963)
4) R. S. Tse, *Combust. Flame.*, **18**, 357 (1972)
5) V. Ya. Shtern, "The Gas-phase Oxidation of Hydrocarbons", translated M. F. Mullins, edited B. P. Mullins, p. 564, Pergamon, Oxford (1960)
6) J. M. Ray and D. J. Waddington, *J. Amer. Chem. Soc.*, **90**, 7176 (1968)
7) H. J. Lucas, A. N. Prater and R. E. Morris, *J. Amer. Chem. Soc.*, **57**, 723 (1935)
8) K. C. Salooja, *Combust. Flame.*, **11**, 320 (1967)

the high temperatures by use of the flow method. It has been found that the principal reaction products are acetaldehyde and butadiene[7].

In the preceding paper[9], it has been shown that the isochor curves of *trans*-butene—2-oxygen mixtures have a low temperature peninsula and show the curve of type III. It has also been suggested that acetaldehyde is an intermediate of the reaction caused in this peninsula.

The experimental results refer to the *trans*-butene-2 (T2B)—oxygen system in the hot ignition region. The present report describes a detailed study of the reaction during the induction period of the explosion. Emphasis is placed on the detection of the intermediates of this reaction. It seems of interest to see whether acetaldehyde is an intermediate and to compare the results with those concerning the other types of combustion.

Experimentals

Materials

T2B and oxygen used were obtained from Takachio Kagaku Co., Ltd., in research grade purities of 99 and 99.99%, respectively. T2B was frozen under liquid nitrogen and degassed before use by trap-to-trap vacuum distillation. Oxygen was taken out from the cylinder and used without further purification.

Apparatus and procedure

The apparatus and procedure used in the present work were similar to those described previously[10]. The progress of the reaction was investigated in the two ranges of the composition of T2B. The reaction products were examined during the induction period at 480°C in the case of 40 vol% of T2B and at 430°C in the case of 50 vol% of T2B. For there appears a low temperature peninsula at temperatures below *ca.* 490°C in the former case and at temperatures below *ca.* 450°C in the latter case[11].

The extent of this reaction was followed by the measurement of total pressure change, using a strain gauge. Then, carrying out a series of runs and interrupting at appropriate time intervals during the induction period, the major products were analyzed quantitatively by means of gas chromatography.

Analysis

After the reaction, using a Toepler pump, the reactants and products were collected and analyzed quantitatively by means of gas chromatography. Carbon monoxide, oxygen and methane were analyzed on a 2 m molecular sieve 5 A column at 66°C, $C_2 \sim C_4$ olefins on a 6 m β, β'-ODPN column

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[9] A. Otani, *Nippon Kagaku Kaishi* (*J. Chem. Soc. Japan Chem. and Ind. Chem.*), 756 (1975)

[10] A. Otani, *Anzen Kogaku* (*J. Japan Soc. Safe Eng.*), **13**, 73 (1974)

[11] A. Otani, *ibid.*, **13**, 367 (1974)

at 48°C and aldehydes on a 2.75 m triacetin column at 48°C. Analysis was mainly performed for gaseous products but it was not done for solid and liquid products. The products except for those described below were also identified.

Results

The consumption of the reactants, the formation of reaction products and total pressure change at various stages of the induction period and after the occurrence of the explosion are shown in Figs. 1 and 2 for the mixture of 50 vol% of T2B with oxygen at 430°C. The findings are expressed as partial pressure in the reaction vessel in mmHg unit at the reaction temperature.

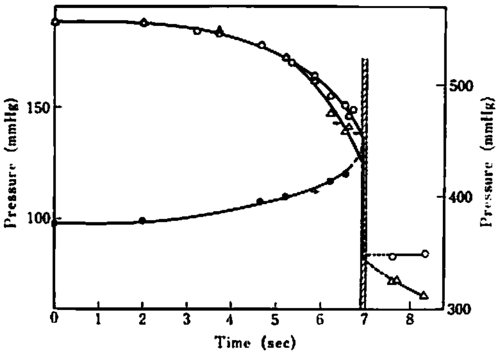


Fig. 1 Progress of the reaction
Temperature 430°C △: oxygen,
○: T2B, ●: total pressure

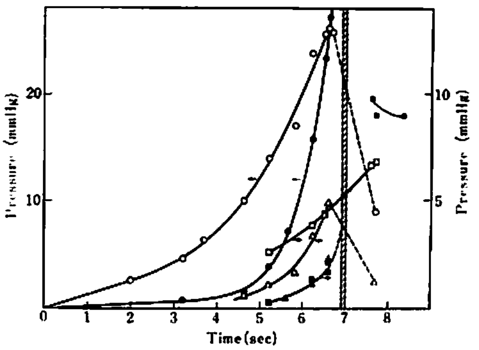


Fig. 2 Product-time curves
Temperature 430°C ○: acetaldehyde,
△: acrolein, ●: carbon monoxide,
□: butadiene, ■: propylene (×2),
▲: methane

Sudden rises or falls of the curves at about 7 seconds show the occurrence of the explosion. The increase of total pressure roughly corresponds to the time of rapid consumption of the reactants. Considerable amounts of the reactants are consumed by the end of the induction period. The consumption of oxygen coincides with that of T2B from the time of admittance to the reaction vessel to about 5 seconds, and then the former becomes larger than the latter.

The first detectable product is acetaldehyde. It should be noted that this is in disagreement with the observations of Norrish and Blundell. The concentrations of acetaldehyde and acrolein increase continuously throughout the induction period, each of which reaches a maximum at the end of this period, and then the occurrence of the explosion results in sudden decrease in their concentrations. Whereas, the occurrence of the explosion results in the steep increase in the concentrations of methane, propylene, butadiene and carbon monoxide. The amount of butadiene is larger than that of acrolein throughout the induction period. Acetaldehyde is the most prominent product throughout this period. These facts show that acetaldehyde is formed as the major intermediate.

The data of Figs. 3 and 4 which refers to a mixture of 40 vol% of T2B at 480°C, shows that again acetaldehyde is formed as the major intermediate. The behavior of the products throughout the induction period and after the explosion is almost similar to that at 480°C. It should be noted, however, that the first detectable products are acetaldehyde and butadiene, and that the occurrence of the explosion results in the decrease in the concentrations of butadiene and propylene. Furthermore, the ratio of acetaldehyde/acrolein is smaller than that at the lower temperature. In addition to the products shown, qualitative analysis after the explosion also reveals that hydrogen, propane and carbon dioxide are produced and detected.

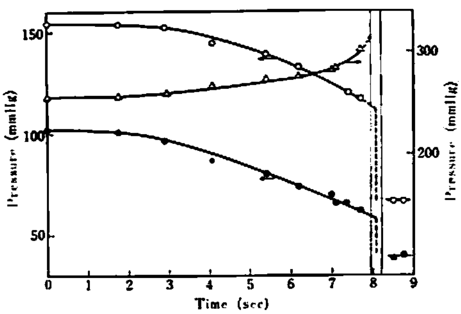


Fig. 3 Progress of the reaction
Temperature 480°C ○: oxygen,
●: T2B, △: total pressure

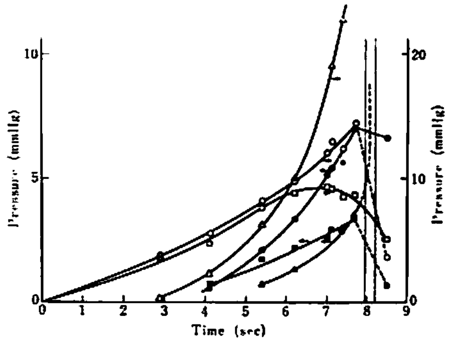
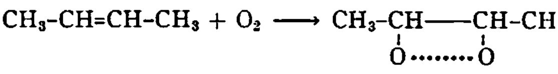


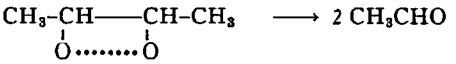
Fig. 4 Product-time curves
Temperature 480°C ○: acetaldehyde,
■: acrolein, △: carbon monoxide,
□: butadiene, ●: propylene (×2),
▲: methane

Discussion

The results described here represent an initial attempt at a detailed study of the explosion reaction of T2B during the induction period. Acetaldehyde is the major intermediate. This fact indicates that the major intermediate of the explosion reaction in the hot ignition region is identical with that of the slow combustion[2~4]. It is confirmed that acetaldehyde is the intermediate of the reaction caused in the low temperature peninsula and plays a role in the isochor curves of type III[9], because the point for this admission pressure at 480°C lies in the low temperature peninsula[11].

The discrepancy between the present results and those of Blundell[2] and Norrish[3] is probably explained on the basis of the difference in the temperatures. The production of acetaldehyde would be accounted for in terms of reaction schemes (1) and (2).


$$\mathrm{CH_3\text{-}CH{=}CH\text{-}CH_3 + O_2 \longrightarrow \begin{array}{c} CH_3\text{-}CH\text{——}CH\text{-}CH_3 \\ \quad\;\; | \qquad\quad | \\ \quad\;\; O\cdots\cdots O \end{array}} \qquad (1)$$


$$\mathrm{\begin{array}{c} CH_3\text{-}CH\text{——}CH\text{-}CH_3 \\ \quad\;\; | \qquad\quad | \\ \quad\;\; O\cdots\cdots O \end{array} \longrightarrow 2\,CH_3CHO} \qquad (2)$$

That is, cycloperoxide would be formed on the direct addition of oxygen molecule across the double bond of T2B, and then immediately would decompose into acetaldehyde. This reaction mechanism has been postulated as a source of acetaldehyde by Neuman[5] and Morris[9].

The mechanism proposed by Morris⁷⁾ for the production of butadiene involving the decomposition of 2, 3-epoxybutane is not compatible with the fact that the first detectable products are acetaldehyde and butadiene at 480°C. It is considered that the decomposition of T2B will occur at the high temperatures. Butadiene produced during the induction period, together with propylene can be explained reasonably on the basis of the decomposition mechanism described as follows.

$$\mathrm{CH_3\text{-}CH{=}CH\text{-}CH_3 + H\cdot \longrightarrow H_2 + CH_3\text{-}CH{=}CH\text{-}CH_2\cdot} \qquad (3)$$

$$\mathrm{CH_3\text{-}CH{=}CH\text{-}CH_2\cdot \longrightarrow CH_3\text{-}\underset{\bullet}{C}H\text{-}CH{=}CH_2} \qquad (4)$$

$$\mathrm{CH_3\text{-}\underset{\bullet}{C}H\text{-}CH{=}CH_2 \longrightarrow CH_2{=}CH\text{-}CH{=}CH_2 + H\cdot} \qquad (5)$$

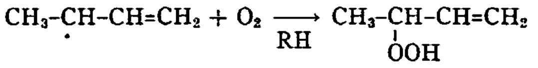
$$\mathrm{CH_3\text{-}\underset{\bullet}{C}H\text{-}CH{=}CH_2 + CH_3\text{-}CH{=}CH\text{-}CH_3 \longrightarrow CH_2{=}CH\text{-}CH{=}CH_2 + CH_3\text{-}\underset{\bullet}{C}H\text{-}CH_2\text{-}CH_3} \qquad (6)$$

$$\mathrm{CH_3\text{-}\underset{\bullet}{C}H\text{-}CH_2\text{-}CH_3 \longrightarrow CH_3\text{-}CH{=}CH_2 + CH_3\cdot} \qquad (7)$$

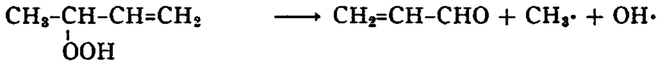
$$\mathrm{CH_3\text{-}CH{=}CH\text{-}CH_3 + CH_3\cdot \longrightarrow CH_4 + CH_3\text{-}CH{=}CH\text{-}CH_2\cdot} \qquad (8)$$

As postulated by Blundell²⁾, the butene-2-1-yl radicals formed by reaction (3) will isomerize to the butene-1-2-yl form before further oxidation occurs. Butadiene in all cases is detected in larger amounts than propylene. Reaction (5) would occur more rapidly than reaction (6). The decomposition of T2B at 480°C occurs more rapidly than at 430°C. This is consistent with the fact that butadiene is the first detectable product at 480°C. The occurrence of the explosion results in the increase of the concentrations of the butadiene and the propylene at the lower temperature. This fact will be explained in terms of consideration that the decomposition of T2B is accelerated by the temperature rise accompanied by the explosion. Whereas, at the higher temperature, the more temperature rise accompanied by the explosion will cause the decomposition of the butadiene and the propylene.

After about 4 seconds, acrolein appears in the products and becomes detectable. The formation of acrolein can be explained on the basis of the reaction mechanism proposed by Blundell²⁾.



$$\mathrm{CH_3\text{-}\underset{\bullet}{C}H\text{-}CH{=}CH_2 + O_2 \xrightarrow[RH]{} CH_3\text{-}\underset{OOH}{\underset{|}{C}}H\text{-}CH{=}CH_2} \qquad (9)$$



$$\mathrm{CH_3\text{-}\underset{OOH}{\underset{|}{C}}H\text{-}CH{=}CH_2 \longrightarrow CH_2{=}CH\text{-}CHO + CH_3\cdot + OH\cdot} \qquad (10)$$

Reaction (9) is the reaction of oxygen with the butene-1-2-yl radicals formed according to reaction (4). As stated by Blundell²⁾, an alternative mode of decomposition of the peroxide will give acetaldehyde. It is considered that this reaction is another possible route for the formation of some parts of the acetaldehyde in the subsequent stages of the induction period. The amount of butadiene is larger than that of acrolein. This fact suggests that reaction (5) occurs more rapidly than reaction (9). That is, the decomposition of the butene-1-2-yl radical occurs more rapidly than the addition of oxygen to this radical. A combination of the above schemes accounts for the important products during the induction period.

The sudden rise in pressure must be associated with the decomposition and degradation of intermediates formed during the induction period. This rise is largely due to the degenerate branching of the acetaldehyde[2,3].

$$CH_3CHO + OH\cdot \longrightarrow H_2O + CH_3CO\cdot \qquad (11)$$

$$CH_3CO\cdot \longrightarrow CH_3\cdot + CO \qquad (12)$$

$$CH_3CO\cdot + O_2 \xrightarrow[RH]{} CO_2 + CH_3\cdot + OH\cdot \qquad (13)$$

Acetaldehyde is the most prominent product throughout the induction period. Therefore, it seems reasonable to conclude that the decomposition of T2B is a side reaction, and that the explosion reaction of T2B largely takes place according to reactions (1), (2), (11)~(13).

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