The Review of Physical Chemistry of Japan Vol. 48 No. 2 (1978)

EXPLOSION REACTION OF OLEFINS

BY AKIRA OTANI

The reaction mechanism is discussed on the basis of the relations between the explosion limits and the molecular structure. At the higher temperatures above *ca* 510°C, it is reasonably concluded that the initiation controls the explosion limits of olefins. Namely, the formation of OH radical according to the addition of an oxygen molecule to the C=C bond under around the equimolar composition, and the hydrogen abstraction by an oxygen molecule in the excess of oxygen, determine the explosion limits.

The isochor curves of $C_2 \sim C_5$ monoolefins at 50 and 60 vol % of oxygen can be grouped into three classes (type I, II and III) as shown in Table 1. It is suggested that acetaldehyde plays an important role in the shape of type III, and a co-operation between HCHO or CH_3CHO and higher aldehydes makes an important contribution to the shape of type II. In the case of olefins belonging to type II and III, the branching of aldehydes formed in the earlier stages at the lower temperatures below *ca* 480°C controls the explosion limits.

Introduction

Although the gas-phase oxidation of several olefins has been studied individually[1~16], a little effort has been expended on comparative studies to establish relationships between the molecular structure and oxidation behavior of these compounds. Waddington *et al.*[17] have investigated the oxidation of trans-2-butene, 2-methyl-2-butene and 2, 3-dimethyl-2-butene at 277°C. They have shown that the initial rate of oxidation of them increases with the number of methyl groups adjacent to the

---

(*Received June, 1978*)

1) J. D. Mullens and G. Skirrow, *Proc. Roy. Soc.*, (*London*), **A244**, 312 (1958)
2) A. Blundell and G. Skirrow, *ibid.*, **A244**, 331 (1958)
3) G. Skirrow, *ibid.*, **A244**, 345 (1958)
4) V. Ya. Shtern, "The Gas-phase Oxidation of Hydrocarbons", translated by M. F. Mullins, edited by B. P. Mullins, Chap IX, Pergamon Oxford (1960)
5) C. F. Cullis, A. Fish and D. W. Turner, *Proc. Roy. Soc.*, (London), **A262**, 318 (1961), **A267**, 433 (1962)
6) G. Skirrow and A. Williams, *ibid.*, **A268**, 537 (1962)
7) R. G. W. Norrish, F. R. S. and K. Porter, *ibid.*, **A272**, 164 (1963)
8) J. H. Knox and C. H. J. Wells, *Trans. Faraday. Soc.*, **59**, 2786, 2801 (1963)
9) E. R. White, H. G. Davis and E. S. Hammack, *J. Amer. Chem. Soc.*, **87**, 1175 (1965)
10) J. L. Franklin, *Ann. Rev.Phys. Chem.*, **17**, 261 (1966)
11) D. J. M. Ray and D. J. Waddington, *J. Amer. Chem. Soc.*, **90**, 7176 (1968)
12) J. H. Jones, T. E. Daubert and M. R. Fenske, *IEC Process. Design and Develop.*, **8**, 196 (1969)
13) R. S. Tse, *Combust. Flame.*, **18**, 357 (1972)
14) D. J. M. Ray and D. J. Waddington, *J. Phys. Chem.*, **76**, 3319 (1972)
15) R. R. Baker, R. R. Baldwin, A. R. Fuller and R. W. Walker, *J. Chem. Soc. Faraday I.*, **71**, 736 (1975)
16) R. R. Baker, R. R. Baldwin and R. W. Walker, *ibid.*, **71**, 736, 756 (1975)
17) D. J. M. Ray and D. J. Waddington, *Combust. Flame.*, **21**, 327 (1973)

carbon-carbon double bond. Salooja[18] has also studied the preflame and ignition behavior of ethylene, propene, butenes and 1-hexene at atmospheric pressure in a flow system. He has found that the observed relative order of the easiness of combustion reaction agrees with the relative order of knocking tendencies in engines. These results have not sufficiently revealed the relationships between the molecular structure and the easiness of oxidation.

While, several investigators have determined the explosion limits of ethylene[19,20], propene[21], propenal[21], vinyl chloride[22], monovinyl acetylene[23] and butadiene[24] mixed with oxygen or air. These results have suggested that these explosions except for the reaction in the region of a high temperature peninsula are thermal in nature. No study has so far carried out under the experimental conditions which can best reveal the influence of molecular structure on the explosion limits.

In order to study the influence of molecular structure on the explosion limits of olefins, we have measured the explosion limits of butenes[25] mixed with oxygen and those of C_5 monoolefins and $C_3 \sim C_5$ dienes[26] under around the equimolar composition with oxygen by means of the admission method. It has already been reported that there exist good relationships between the explosion limits and their molecular structure.

We have now investigated the effect of addition of small amounts of aldehydes on the explosion reaction and the extent of the explosion reaction of the butenes, in order to obtain further useful information as to the reaction mechanism. At first, we will describe in detail the effect of molecular structure on the explosion limits. Secondly, the reaction mechanism will be discussed in view of a new standard by use of the relationships and the data here. A plausible reaction mechanism for the explosion reaction of the olefins will be proposed.

Experimentals

The experimental apparatus and procedure have already been reported elsewhere in detail[25]. The reaction vessel consisted essentially of silica glass with a length of 150mm and a diameter of 30mm. The criterion used for a explosion was the sharp pressure rise noted on the chart of a pen-oscillograph and the observation of flame through a mirror. The effect of addition of small amounts of aldehydes on the explosion limits and on the induction period has been examined. The extent of the explosion reaction at the composition 40 vol % of 1-butene and trans-2-butene has also investigated by use of a similar method to that described previously[27].

---

18) K. C. Salooja, *Combust. Flame*, **11**, 320 (1967), **12**, 401 (1968)
19) M. Suga, *This journal*, **28**, 67 (1958)
20) M. Suga, *Bull. Chem. Soc. Japan.*, **31**, 515 (1958), **32**, 425 (1959)
21) S. Kusuhara, *This Journal*, **30**, 34 (1960)
22) M. Suga, *ibid.*, **29**, 73 (1959)
23) T. Ikegami, *ibid.*, **31**, 13 (1962), **33**, 6 (1963)
24) J. Osugi, H. Kubota and K, Ueba. *ibid.*, **35**, 38 (1965)
25) A. Otani, *Anzen Kogaku* (*J. Japan. Soc. Safety. Eng.*), **13**, 73, 136, 367 (1974)
26) A. Otani, *Nippon Kagaku Kaishi* (*J. Chem. Soc. Japan, Chem. and Ind. Chem.*), **1975**, 756, 948
27) A. Otani, *This Joural*, **46**, 82 (1976)

Results and Discussion

Effect of molecular structure on the explosion reaction

Townend *et al.*[28,29] have reported that the isochor curves of hydrocarbon-air mixtures under high pressure except for coolflame region can be grouped into three classes in terms of the number of carbon atoms. Fig. 1 shows the schematical representation of these three curves. Here, each of them is named "type I", "type II" and "type III". Namely, the curve of type I is smooth and the pressure of explosion limit decreases continuously with temperature. The curve of type II has typical pressure at which the pressure of explosion limit is independent of temperature. Namely, there is a sharp break in the isochor curve. The curve of type III has the three temperature limits with respect to pressure. That is, there is a low temperature peninsula of the explosion limit.

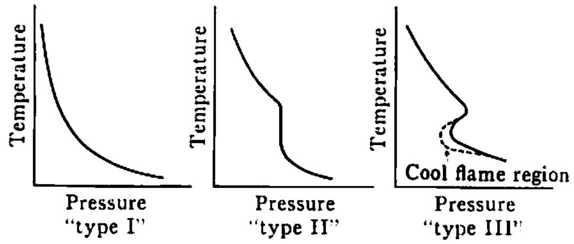


Fig. 1 Schematic representation of the regions of explosion limits

The shapes of the isochor curves of the butenes at the lower temperatures below *ca* 480°C are dependent on their molecular structure, as shown in Fig 2. The explosion limits of C_2~C_5 mono-

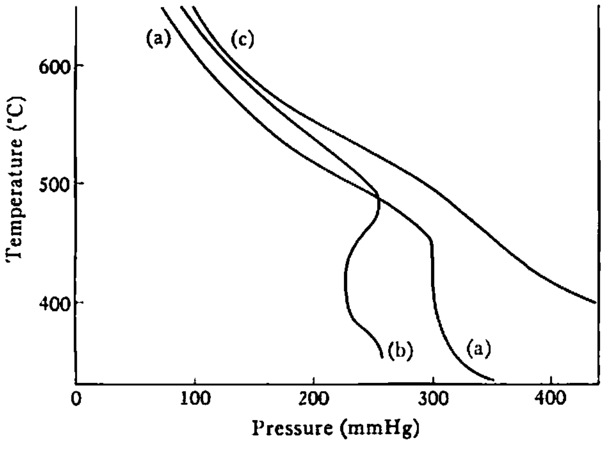


Fig. 2 Isochor curves of butenes
(a) 1-butene (50 vol% of O_2),
(b) trans-2-butene (60 vol% of O_2),
(c) 2-methyl propene(60 vol% of O_2).

---

[28] G. P. Kane and D. T. A. Townend, *Proc. Roy. Soc*, (London), A160, 174 (1937)
[29] D. T. A. Townend, *Chem. Rev.*, 21, 259 (1938)

olefins and $C_3\sim C_5$ dienes mixed with oxygen are compared among each other at the compositions of 50 and 60 vol% of oxygen at pressures below about 500mmHg. It has been found that all the isochor curves can be grouped into these three classes, as summarized in Table 1. Especially, the shape of the isochors below *ca* 480°C determines this classification. All the isochors of the dienes show the curve of type I. On the other hand, alkanes mixed with oxygen except for methane give the curve of type III[30].

The effects of substituents on the shapes of the isochor curves of $C_2\sim C_5$ monoolefins are discussed on the basis of the results. The replacement of one hydrogen atom in ethylene by ethyl or *n*-propyl group leads to a change from type I to type II. The substitution of two hydrogen atoms on one carbon atom keeps the shape of the curve as type I, while the substitution of two hydrogen atoms on adjacent carbon atoms results in a change from type I to type II or type III. These facts suggest that the cleavage at the C=C bond plays an important role in the explosion reaction. Three isomers of the butenes give the three different isochor curves. Therefore, this classification can not be explained in terms of the number of carbon atoms as proposed by Townend[28, 29].

Table 1 Classification of the isochor curves

Type I	Type II	Type III
Ethylene, Isoprene	1-butene	Trans-2-butene
2-methyl-1-butene	1-pentene	Cis-2-butene
Vinyl chloride	2-pentene	Propene
2-methyl propene	2-methyl-	
Propadiene	2-butene	
1.3-butadiene		
1.3-pentadiene		
Monovinyl acetylene		

Aldehydes have been recognized as chain branching intermediates in the combustion of hydrocarbons. For example, Norrish *et al.*[7] have reported that acetaldehyde is a major intermediate in the low temperature oxidation of 2-butene. Then, the effect of addition of small amounts of aldehydes on the explosion of the butenes has been examined. The aldehydes are formaldehyde, acetaldehyde, propanal and propenal, which have been confirmed to be formed in the low temperature oxidation of the butenes[2, 3, 6, 7, 18].

Figs. 3, 4 and 5 show the results for 1-butene. All the aldehydes reduce the induction period of the explosion. The magnitude of this effect at 550°C increases in the order, $HCHO<CH_3CHO<C_2H_5CHO<CH_2=CHCHO$. Salooja[31] has found that the ignition temperature increases in the order, $CH_2=CHCHO<C_2H_5CHO<CH_3CHO<HCHO$. One can find that there exists a good correlation

---

[30] C. H. Bamford and C. F. H. Tipper, "Comprehensive Chemical Kinetics", Vol 17, Elsevier, New York (1977)

[31] K. C. Salooja, *Combust. Flame*, **9**, 373 (1965)

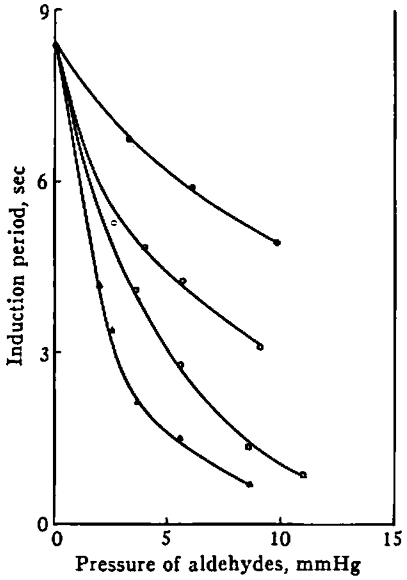


Fig. 3 Effect of addition of aldehydes on the induction period of explosion reaction of 1-butene at 550°C (1-butene: 56mmHg, oxygen: 84mmHg)
△: propenal, □: propanal,
○: acetaldehyde,
● :formaldehyde

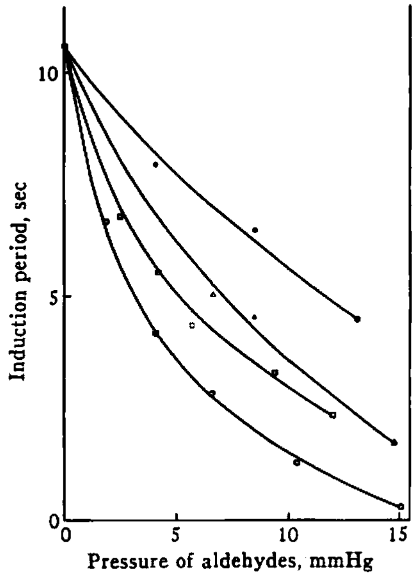


Fig. 4 Effect of addition of aldehydes on the induction period of explosion reaction of 1-butene at 470°C (1-butene: 100mmHg, oxygen: 150mmHg)
△: propenal, □: propanal,
○: acetaldehyde,
●: formaldehyde

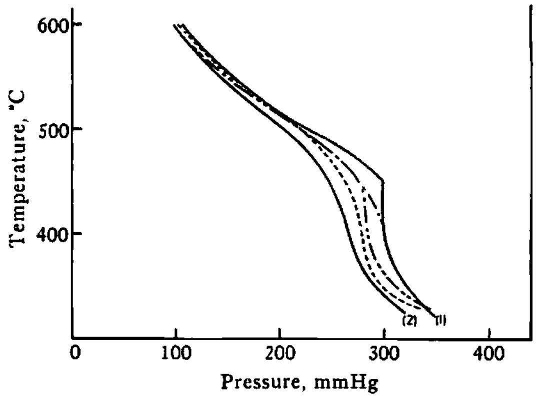


Fig. 5 Effect of addition of aldehydes on the explosion limits of 1-butene(50 vol%) -oxygen mixture (aldehyde: 1.4 vol%)
—·— propenal, - - -: propanal,
—··—: formaldehyde,
(1): 0, (2): acetaldehyde

between the order of this effect and their ignition temperatures. While, the magnitude of this effect at 470°C increases in the order, $HCHO<CH_2=CHCHO<C_2H_5CHO<CH_3CHO$. This order is different from that at 550°C. There exists another correlation between the order of this effect and the respective reactivity of aldehydes reported by Salooja31), who has found that the reactivity of al-

dehydes increases in the order, $HCHO < CH_2{=}CHCHO < C_2H_5CHO < CH_3CHO$. This order is also consistent with that of easiness of the initiation of the gas-phase oxidation of aldehydes[30,32,33]. Namely, the initiation increases in the order at 440°C, $HCHO < C_2H_5CHO < CH_3CHO$.

The effect of addition of aldehydes on the explosion limit at the higher temperatures above *ca* 500°C is small, while, the aldehydes except for propenal reduce largely the pressure of explosion limit at the lower temperatures below *ca* 480°C. The order of this effect is consistent with that of the effect on the induction period. The results indicate that aldehydes play an important role in the explosion reaction at the lower temperatures. These facts have suggested that this classification can be made in terms of aldehydes assumed as intermediates in the explosion reaction.

In order to confirm this, the extent of the reaction in the low temperature peninsula has been investigated for a trans-2-butene-oxygen mixture[27]. This result has indicated that acetaldehyde is a major intermediate and it makes an important contribution to the shape of type III.

The pressures of explosion limit of $C_2 \sim C_5$ monoolefins at the higher temperatures above *ca* 500°C have also been compared among each other under around the equimolar composition rather than the stoichiometric one for complete oxidation. The pressures of explosion limit of $C_2 \sim C_4$ monoolefins increase in the order, ethylene<1-butene<2-butene<propene<2-methyl propene. Although the explosion of ethylene occurs more readily than 1-butene, the easiness of explosion of other olefins is consistent with that of oxidation observed by Salooja[18], who has found that the easiness of oxidation increases in the order, 2-methyl propene<propene<ethylene<2-butene<1-butene. Contrary to the observation of Norrish and Porter[7], the explosion of 1-butene occurs more readily than 2-butene. The pressure of explosion limit of 2-methyl-2-butene is lower than that of trans-2-butene. This agrees with the order of the initial rate obtained by Waddington *et al.*[17] at 277°C. The effects of substituents on the pressures of explosion limit are discussed on the basis of the results. The substitution of hydrogen atoms in ethylene results in a rise of the pressures of explosion limit. In each case of the olefins studied with structures $RHC{=}CH_2$, $RR'C{=}CH_2$ and $RHC{=}CHR'$, the explosion occurs more readily as the alkyl group is lengthened. The pressures of explosion limit of $RHC{=}CH_2$ are the lowest in the olefins having the same number of carbon atoms.

Bellamy *et al.*[34] have found that the C=C stretching frequencies of non-conjugated olefins are related to the enthalpies of hydrogenation. The possibility of a relation between the pressures of explosion limit and the corresponding C=C stretching frequencies has been considered. It has been found that there exists a good correlation at temperatures 530°, 550° and 600°C, as shown in Fig. 6. A relation similar to that in Fig. 6 holds for 50 vol% of oxygen. The pressures of explosion limit increase as the C=C frequency rises. While, the exothermicities of hydrogenation decrease as the C=C frequency rises, as shown by Bellamy[34]. It should be noted that the data for trans-2-butene and 2-methyl-2-butene do not lie on the curves in Fig. 6. It is suggested that this is due to the steric effect.

---

32) R.R. Baldwin, A. R. Fuller, D. Longthorn and R. W. Walker, *J. Chem. Soc. Faraday I.*, 70, 1257(1974)

33) R. R. Baldwin, R.W. Walker and D. H. Langford, *Trans. Faraday Soc.*, **65**, 792, 806 (1969)

34) L. J. Bellamy and R. L. Williams., *J. Chem. Soc.*, **1958**, 2463

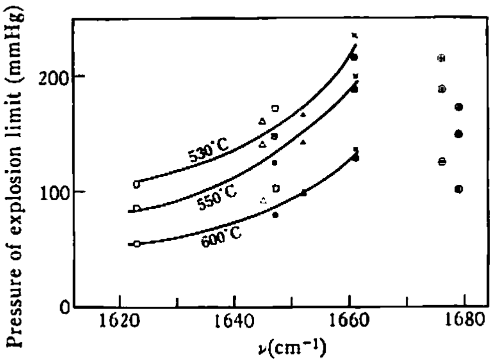


Fig. 6 Relation between the pressures of explosion limits and the corresponding stretching frequencies of the C=C bond
(composition: 60vol% of O_2)
○: ethylene, △: 1-butene,
●: 1-pentene, □: propene,
▲: 2-methyl-1-butene,
■: cis-2-butene, ×: 2-methyl propene
◎: 2-methyl-2-butene,
◉: trans-2-butene

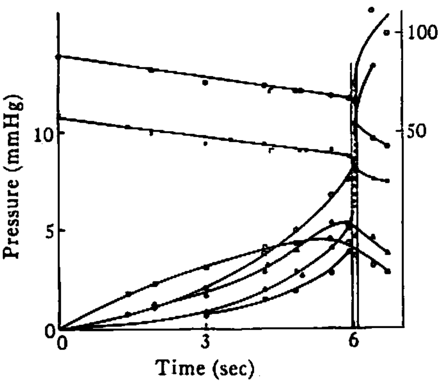


Fig. 7 Explosion reaction of 1-butene at 550°C (Initial pressure: 1-butene, 59mmHg, oxygen, 89mmHg)
○: ethylene, □: butadiene,
△: propene, ●: methane,
▲: carbon monoxide x 0.2,
×: 1-butene, ◎: oxygen.

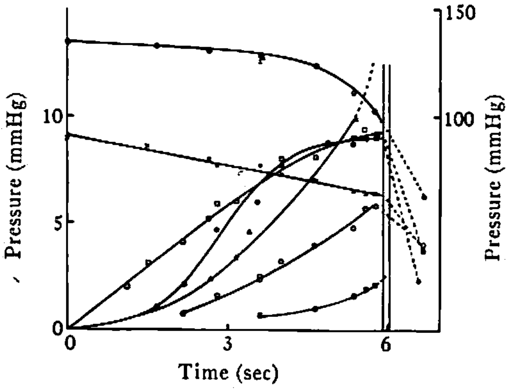


Fig. 8 Explosion reaction of trans-2-butene at 530°C
(Initial pressure: trans-2-butene, 90mmHg, oxygen, 136mmHg)
■: ethylene, ○: propene,
□: butadiene, ◎: oxygen
△: carbon monoxide x 0.5,
●: acetaldehyde, ×: trans-2-butene.

In order to explain this discrepancy, the extent of the reaction has been investigated for 1-butene and trans-2-butene at 60 vol% of oxygen. Figs. 7 and 8 show the results. Contrary to the observation of Baldwin *et al.*16), the amount of butadiene from trans-2-butene is larger than that from 1-butene. However, this is consistent with the observation of Fenske *et al.*12) The consumption of trans-2-butene is larger than that of oxygen in the earlier stages, while the consumption of 1-butene is equal to that of oxygen.

At the compositions more than 90 vol% of oxygen, it has been found that a relationship exists between the dissociation energies of a carbon-hydrogen bond at α-position and the pressures of explosion limit of $C_2 \sim C_4$ monoolefins, as shown in Fig. 9. However, it should also be noted that the data for trans-2-butene do not lie on the curves in Fig. 9. The data for *n*-butane and isobutane lie on

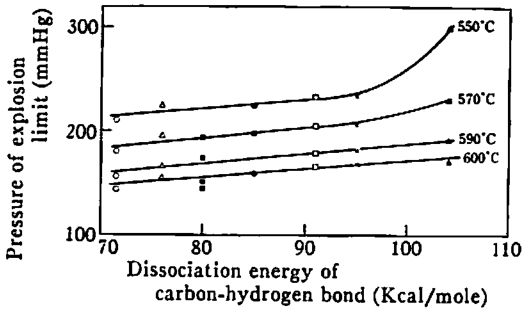


Fig. 9 Relation between the pressures of explosion limit and dissociation energies of carbon-hydrogen bond (composition: 90 vol% of O_2)
○: 1-butene, △: 2-methyl propene,
■: trans-2-butene, ●: propene,
□: isobutane, ×: *n*-butane,
▲: ethylene.

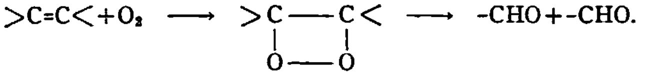
the curves. This fact suggests that the abstraction of a hydrogen atom at α-position plays an important role in the explosion reaction.

It is reasonably concluded that the easiness of explosion reaction above *ca* 510° C is reflected directly by the nature of a molecular bond, and that the reaction mechanism for the monoolefins-oxygen mixtures varies with the composition of oxygen at the higher temperatures.

Reaction mechanism

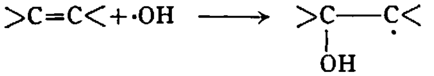
Numerous studies of the gas-phase oxidation of olefins at the low temperatures below 400°C have shown that carbonyl compounds and epoxides are the principal products[1~14]. It has generally been accepted that the carbonyl compounds (mainly aldehydes) are formed according to four kinds of reaction schemes described below.

(i) Decomposition of a dioxetane formed by the direct addition of an oxygen molecule to the C=C bond

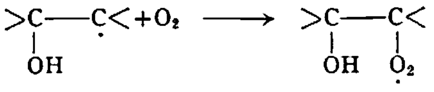


$$>C{=}C< + O_2 \longrightarrow \begin{array}{c}>C - C<\\ |\qquad|\\ O - O\end{array} \longrightarrow -CHO + -CHO. \qquad (1)$$

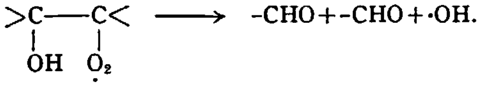
(ii) Consecutive addition reactions with a hydroxyl and oxygen



$$>C{=}C< + \cdot OH \longrightarrow \underset{OH}{>C} - \dot{C}< \qquad (2)$$



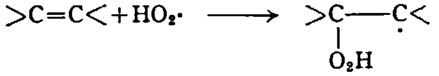
$$\underset{OH}{>C} - \dot{C}< + O_2 \longrightarrow \underset{OH}{>C} - \underset{\dot{O}_2}{C}< \qquad (3)$$



$$\underset{OH}{>C} - \underset{\dot{O}_2}{C}< \longrightarrow -CHO + -CHO + \cdot OH. \qquad (4)$$

Recently, Waddington[35] has reported that the hydroxyl radical is more important species in the low temperature region.

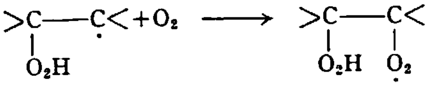
(iii) The reactions involving the addition of a hydroperoxyl radical, followed by the addition of an oxygen molecule



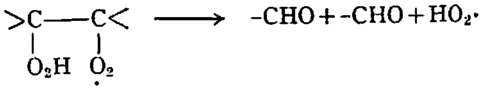
$$>C{=}C< + HO_2\cdot \longrightarrow \underset{O_2H}{>C} - \dot{C}< \qquad (5)$$

---

35) D. J. M. Ray, A. Redfearn and D. J. Waddington, *J. Chem. Soc. Perkin Trans II.*, **1973**, 540



$$>\underset{O_2H}{\underset{|}{C}}-\underset{\cdot}{C}<+O_2 \longrightarrow >\underset{O_2H}{\underset{|}{C}}-\underset{\underset{\cdot}{O_2}}{\underset{|}{C}}< \qquad (6)$$



$$>\underset{O_2H}{\underset{|}{C}}-\underset{\underset{\cdot}{O_2}}{\underset{|}{C}}< \longrightarrow -CHO+-CHO+HO_2\cdot \qquad (7)$$

(iv) Formation of peroxide by the addition reaction of an oxygen molecule to a radical produced by abstraction of a hydrogen atom and its subsequent decomposition

$$RH+O_2 \longrightarrow R\cdot \xrightarrow{O_2} ROO\cdot \xrightarrow{RH} ROOH \rightarrow \text{aldehydes, etc} \qquad (8)$$

It has been reported that aldehydes formed in the earlier stages are considerably more reactive than the parent olefins, and they control the subsequent process of the reaction[36, 37].

(1) ***Higher temperature region (ca 510°~600°C) under around the equimolar composition:*** As described before, it has been found that there exists the relationship between the pressures of explosion limit of $C_2 \sim C_5$ monoolefins and the corresponding C=C stretching frequencies. This result has suggested that the C=C bond plays an important role in the explosion.

The reactions involving the C=C bond have been generally accepted to be addition of an oxygen molecule, a hydroxyl or a hydroperoxyl radical. Namely, reaction (1) is an important initial step and reactions (2)~(4) and (5)~(7) are important propagating steps. Knox[38] has shown that the hydroxyl radical is more important species because the compounds formed by addition of OH radical to the C=C bond are more stable than those of HO_2 radical addition above 470°C. Therefore, it is considered that reactions (2)~(4) are more important propagating steps in the explosion reaction.

Kinetic data for the reaction between simple olefins and OH radical have been reported by Pitt *et al.*[39, 40] in the temperature range 24~152°C. The rate constants of reaction (2) and the enthalpy changes of reactions (2)~(4) can be estimated by use of Arrhenius parameters for $C_2 \sim C_4$ olefins and the group additivity[41, 42], as given in Table 2 and 3.

Table 2 Rate constants of OH radical additions at 550°C and enthalpy changes (ΔH_2°)

Olefin	k(cm^3 mol^{-1} sec^{-1})	ΔH_2° (Kcal mol^{-1})
ethylene	2.1×10^{12}	-32.4
propene	4.8×10^{12}	-33.2
1-butene	8.1×10^{12}	-33.2
2-methyl propene	1.0×10^{13}	-34.8
cis-2-butene	1.1×10^{13}	-34.2
trans-2-butene	1.3×10^{13}	-34.2

---

36) R. R. Diaz, K.Seldy and D. J. Waddington, *J. Chem. Soc. Perkin. Trans II.*, **1975**, 758
37) K. Selby and D. J. Waddington, *ibid.*, **1975**, 1715
38) J. H. Knox, *Combust. Flame*, **9**, 297 (1965)
39) R. Atkinsn and J. N. Pitts. Jr, *J. Chem. Phys.*, **63**, 3591 (1975)
40) R. Atkinsn, R. A. Perry and J. N. Pitts. Jr. *ibid.*, **66**, 1197 (1977)
41) H. E. O'Neal and S. W. Benson. *Int. J. Chem. Kinet.*, **1**, 221, (1969)
42) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw and R. Walsh, *Chem. Rev.*, **69**, 279 (1969)

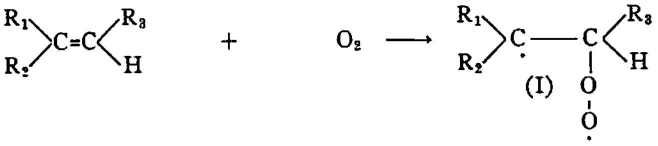
As revealed in Table 2, the rate constant and enthalpy change of ethylene are the smallest in the above olefins. Exothermicities of reaction (3) are almost equal to each other and about 27 Kcal mol^{-1}. The exothermicity of reaction (4) with respect to ethylene is also the smallest. On the other hand, the pressure of explosion limit of ethylene is the lowest. It is concluded reasonably that reactions (2)~(4) do not control the explosion limit though these steps are more important propagating steps. It has been reported that addition of O (^3P) atom to the ethylene occurs most slowly in the olefins and the rate constant of HO_2 addition to the ethylene is smaller than that of 2-methyl propene[43]. These facts suggest that propagating steps do not control the explosion limits.

Table 3 Enthalpy changes of reactions (3) and (4)

Parent olefin	ΔH_3° (Kcal mol^{-1})	ΔH_4°(Kcal mol^{-1})
ethylene	−27.2	−8.4
propene	−27.4	−11.7
1-butene	−27.3	−12.7
2-methyl propene	−26.5	−14.1
trans-2-butene	−27.3	−15.2
cis-2-butene	−27.3	−15.2
1-pentene	−27.3	−11.1

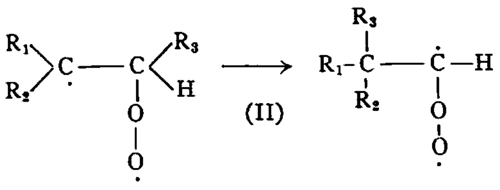
It has been postulated that reaction (1) is an important step. However, Waddington *et al.*[35] have shown that the formation of a dioxetane is highly endothermic ($\Delta H \approx 69$ Kcal mol^{-1}) because this reaction includes a spin-forbidden transition. Therefore, it is suggested that the possibility that reaction (1) is an initial step is very small.

Fenske *et al.*[12] have reported that an initial step is an addition of an oxygen molecule to the C=C bond. This reaction is as follows;



(9)

Here, R_1 and R_2 are alkyl groups or hydrogen atoms, and R_3 is methyl group or hydrogen atom. In the case of unsymmetric olefins, addition of oxygen molecule to the less substituted olefinic carbon atom is favored. The biradical (I) is suggested to be a triplet-state by the spin conservation rule. Therefore, this biradical can not join its end to give cyclic peroxides. This biradical undergoes further reactions (10) and (11).

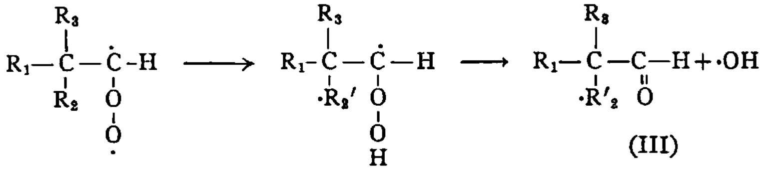


(10)

---

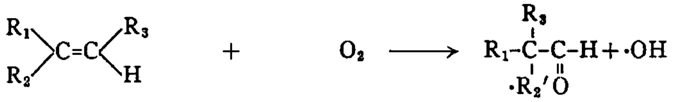
[43] C. H. Bamford, and C. F. H. Tipper, "Comprehensive Chemical Kinetics", vol. 18, Elsevier, New York (1977)

The biradical (II) is formed *via* a 1,2-hydrogen or alkyl migration, as proposed by Cvetanovic[44] in the case of addition of oxygen (^3P) atom to olefins.



$$R_1-\overset{R_3}{\underset{R_2}{C}}-\underset{\substack{O \\ | \\ \dot{O}}}{\dot{C}}-H \longrightarrow R_1-\overset{R_3}{\underset{\cdot R_2'}{C}}-\underset{\substack{O \\ | \\ O \\ H}}{\dot{C}}-H \longrightarrow \underset{\text{(III)}}{R_1-\overset{R_3}{\underset{\cdot R'_2}{C}}-\underset{\substack{\| \\ O}}{C}-H}+\cdot OH \qquad (11)$$

The biradical (II) except for that from ethylene abstracts a hydrogen atom from the alkyl group (R_2) *via* a six member ring transition, and subsequently decomposes to a radical (III) and a OH radical. In the case of ethylene, it is considered that the biradical (II) decomposes to an acetyl and a OH radical. Namely, the most probable initiation is as follows ;



$$\begin{matrix} R_1 & & R_3 \\ & C=C & \\ R_2 & & H \end{matrix} + O_2 \longrightarrow R_1-\overset{R_3}{\underset{\cdot R_2'}{C}}-\underset{\substack{\| \\ O}}{C}-H+\cdot OH \qquad (12)$$

The enthalpy change of reaction (12) and the heat of formation of the radical (III) can be estimated by use of the group additivity[41,43], as given in Table 4.

Table 4 Heat of formation of radical (III) and enthalpy change of reaction (12) (ΔH_{12}°)

olefin	ΔH_{12}° (Kcal mol^{-1})	ΔH_f°(Kcal mol^{-1})
ethylene	−7.2	−4.0
propene	5.7	1.3
1-butene	2.2	−7.3
trans-2-butene	6.2	−5.8
cis-2-butene	5.2	−5.8
2-methyl propene	7.6	−5.8
1-pentene	2.2	−12.1
2-methyl-1-butene	3.8	−14.2

The formation of OH radical from ethylene is exothermic and that from other olefins is endothermic. The endothermicity of reaction(12)increases in the order, ethylene$<$1-butene$=$1-pentene$<$2-methyl-1-butene$<$cis-2-butene$\leq$propene$<$2-methyl propene. This order is almost consistent with that of the pressure of explosion limit. In the case of 1-butene and 1-pentene, reaction (12) for 1-pentene occurs more easily than that for 1-butene since the radical (III) from 1-pentene is more stable than that from 1-butene. These facts suggest that the formation of OH radical by oxygen addition to the C=C bond controls the explosion limits.

The radical (III) is by far more stable than OH radical because the heat of formation of OH radical is endothermicity of 9.3 Kcal mol^{-1}[45] and that of the radical (III) is generally exothermic.

---

[44] R. J. Cvetanovic, *Advan, Photochem.*, **1**, 115 (1963)

[45] J. A. Kerr, *Chem. Rev.*, *66*, 465 (1966)

Therefore, it is suggested that the contribution of OH radical in the propagating steps is more important than that of the radical (III). Carbonyl compounds are formed according to reactions (2)~(4), which are important propagating steps. The carbonyl compounds formed will undergo further branching reactions since these are unstable at the higher temperatures. It is concluded reasonably that the formation of OH radical by oxygen addition to the C=C bond controls the explosion limits.

The amount of butadiene from trans-2-butene is larger than that from 1-butene. The formation of butadiene can be explained on the basis of the reaction mechanism described below.

$$CH_3CH{=}CHCH_3 + O_2 \longrightarrow \dot{C}H_2CH{=}CHCH_3 + HO_2\cdot \qquad (13)$$

$$\dot{C}H_2CH{=}CHCH_3 \longrightarrow CH_2{=}CH\underset{\bullet}{C}HCH_3 \qquad (14)$$

$$CH_2{=}CH\underset{\bullet}{C}HCH_3 + O_2 \longrightarrow CH_2{=}CH\text{-}CH{=}CH_2 + HO_2\cdot \qquad (15)$$

$$CH_3CH{=}CHCH_3 + HO_2\cdot \longrightarrow \dot{C}H_2CH{=}CHCH_3 + H_2O_2 \qquad (16)$$

Since 1-butene undergoes reaction (9) more readily than trans-2-butene because of a steric effect of two methyl groups, the contribution of reaction (13) is more larger in the latter. The pressure of explosion limit of 2-methyl-2-butene is lower than that of trans-2-butene. This agrees with the order of the initial rate of oxidation obtained by Waddington[17], who has explained that this is due to the increasing ability of hydrogen atom abstraction from the methyl groups. This is an alternative explanation for the fact that reaction (13) occurs more easily for trans-2-butene and 2-methyl-2-butene. The data for these olefins do not lie on the curves in Fig. 6. Probably this may be due to the fact that reaction (12) competes with reaction (13).

(2) ***In the case of an excess of oxygen (above 510°C):*** The pressure of explosion limit of ethylene is the highest among C_2~C_4 monoolefins and the substitution of alkyl groups for hydrogen atoms of ethylene results in a fall of the pressure. It has been found that there exists a correlation between the pressure of explosion limit of them and the dissociation energies of a carbon-hydrogen bond at α-position, as shown in Fig. 9. These facts indicate that the easiness of explosion is reflected directly by the nature of the bond of carbon-hydrogen comprising a molecule because intermediates formed in the earlier stages are more unstable than the parent olefins. Namely, it is concluded that the abstraction of a hydrogen atom plays an important role in the explosion. The data for *n*-butane and isobutane lie on the curves in Fig. 9. This is taken as further evidence for which described above.

The results can be explained on the basis of reaction (8). Aldehydes formed in the earlier stages will suffer further oxidation. Namely, the abstraction by an oxygen molecule controls the explosion limits.

It is concluded reasonably, at the higher temperatures above *ca* 510°C, that the formation of OH radical according to the addition of an oxygen molecule to the C=C bond under around the equimolar composition and the abstraction of a hydrogen by an oxygen molecule in the excess of oxygen, determine the explosion limits of the monoolefins.

(3) ***Classification of the isochor curves of the monoolefins under around the equimolar composition:*** As discussed before, the shape of the isochors at the lower temperatures below *ca* 480°C determines this classification. The effect of substituents on the type of the isochors suggests that the cleavage at the C=C bond plays an important role in the explosion reaction. Addition of small

amounts of aldehydes reduces the induction period, and promotes the explosion reaction at the lower temperatures. The magnitude of this effect correlates with respective reactivity of aldehydes. These facts suggest that aldehydes also make an important contribution to the explosion reaction. It is considered that aldehydes are formed by the cleavage at the C=C bond. Namely, aldehydes will be formed according to reactions (12) and (2)~(4).

The rate constant of OH radical to the C=C bond is sufficiently larger than that of hydrogen abstraction from the aldehydes[43] and the amount of olefins is by far larger compared with that of the aldehydes formed. Therefore, the addition of OH radical to the olefins is more favored. The aldehydes formed are considerably stable at the lower temperatures. These facts suggest that aldehydes serve as branching agents.

In the case of the olefins belonging to type I, aldehyde formed by reactions (12) and (2)~(4) is only formaldehyde. The isochor curves of formaldehyde show the curve of type I[4]. These indicate that formaldehyde gives the shape of type I.

With respect to trans-2-butene, it has been found that acetaldehyde is a major intermediate. Although we have reported that acetaldehyde is formed *via* a dioxetane[27], the formation of the acetaldehyde can be explained more reasonably in terms of reactions (12) and (2)~(4) on the basis of the discussion before. It is concluded that acetaldehyde makes an important contribution to the shape of type III. This is consistent with Townend's assumption[28,29].

Except for 2-methyl-2-butene, olefins belonging to type II give HCHO or CH_3CHO and higher aldehydes. The easiness of explosion of these olefins increases in the order, 1-butene<1-pentene< 2-pentene. That of aldehyde increases in the order, $HCHO < C_2H_5CHO < n\text{-}C_3H_7CHO < CH_3CHO$. One can find a good correlation between the easiness of explosion and the reactivity of aldehydes formed. Namely, the easiness of explosion of these olefins can be explained on the basis of branching of aldehydes assumed as intermediates.

Walker *et al.*[32,33,46~49] have reported that the oxidation mechanism of aldehydes is relatively simple and that acetaldehyde is different from other aldehydes because of the singularity of methyl radical. For example, the mechanism for propanal is as follows;

$$C_2H_5CHO + O_2 \longrightarrow C_2H_5\dot{C}O + HO_2\cdot \qquad (17)$$

$$C_2H_5\dot{C}O + M \longrightarrow \dot{C}_2H_5 + CO + M \qquad (18)$$

$$\dot{C}_2H_5 + O_2 \longrightarrow C_2H_4 + HO_2\cdot \qquad (19)$$

$$HO_2\cdot + C_2H_5CHO \longrightarrow C_2H_5\dot{C}O + H_2O_2 \qquad (20)$$

It has been reported that the rate constant of a hydrogen abstraction by a HO_2 radical from formaldehyde is comparable with that from higher aldehydes, and a formyl radical formed is more stable than higher carbonyl radicals[31]. Consequently, formaldehyde is suggested to retard the oxidation of the higher aldehydes as found by Tipper[50].

In the case of 2-pentene, the aldehydes produced by reactions (12) and (2)~(4) are acetaldehyde

---

46) R. R. Baldwin, M. J. Matchan and R. W. Walker, *Combust. Flame*, **15**, 109 (1970)

47) R. R. Baldwin, M. J. Matchan and R. W. Walker, *Trans. Faraday Soc.*, **67**, 3521 (1971)

48) R. R. Baldwin, A. R. Fuller, D. Longthorn and R. W. Walker, *J. Chem. Soc. Faraday I*, **68**, 1362(1972)

49) R. R. Baldwin, R. W. Walker and D. A. York, *ibid.*, **69**, 826 (1973)

and propanal. Walker has shown that acetaldehyde serves as the source of methyl radical. The reaction mechanism is as follows;

$$CH_3CHO+O_2 \longrightarrow CH_3\dot{C}O+HO_2\cdot \qquad (21)$$

$$CH_3\dot{C}O+M \longrightarrow \dot{C}H_3+CO+M \qquad (22)$$

$$\dot{C}H_3+CH_3CHO \longrightarrow CH_4+CH_3\dot{C}O \qquad (23)$$

$$\dot{C}H_3+O_2 \rightleftarrows CH_3O_2\cdot \longrightarrow \text{Oxidation products.} \qquad (24)$$

Using suitable Arrhenius parameters[43, 46], the author calculated the rate constant of the hydrogen abstraction from propanal by methyl radical and its value is comparable with that from acetaldehyde. Namely, the reaction (23) occurs in the competition with reaction (25).

$$\dot{C}H_3+C_2H_5CHO \longrightarrow C_2H_5\dot{C}O+CH_4 \qquad (25)$$

Propionyl radical suffers further reactions (18) and (19). Since the oxidation of acetaldehyde occurs more readily than that of propanal, the easiness of explosion of 2-pentene can be explained in terms of acetaldehyde, but it is considered that acetaldehyde and propanal determine the shape of the isochors. It is reasonably concluded that a co-operation between HCHO or CH_3CHO and higher aldehydes makes an important contribution to the shape of type II.

Finally, all the dienes belong the type I. However, in the case of 1,3-pentadiene, the pressure-time traces indicated clearly that the explosion at lower temperatures below *ca* 410°C occured after the pressures decreased. On the other hand, at higher temperatures above 410°C, the pressure increase was first observed. Therefore, it is necessary to study the reaction mechanism in detail.

Acknowlegement

The author wishes to thank prof. J. Osugi(Kyoto univ.) and Dr. T. Ikegami(Kanegafuchi Chem. Ind. Co., Ltd.) for their guidance and advice throughout this work. He is also grateful to Kanegafuchi Chem. Ind. Co., Ltd. for the admittance of this publication.

Central Research Laboratory
Kanegafuchi Chem. Ind. Co., Ltd.
Kobe 652
Japan

---

50) D. J. Dixon, G. Skirrow and C. F. H. Tipper, *J. Chem. Soc. Faraday I*, 70, 1078, 1090 (1974)