

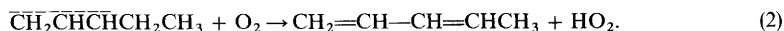
## Addition of Pentenes to Slowly Reacting Mixtures of Hydrogen and Oxygen at 480°C

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A detailed analysis has been made of the products formed when 1% of pent-1-ene and of *cis*-pent-2-ene are added to slowly reacting mixtures of  $H_2 + O_2$  in aged boric-acid-coated vessels at 480°C. The primary products are formed through four different types of attack on the pentenes of almost equal importance, radical addition of H, OH and  $HO_2$ , and H atom abstraction from the pentenes by all three radicals. Penta-1,3-diene is the only  $C_5$  diene observed, in marked contrast to an earlier study of pentene oxidation. From measurements of the initial relative yields of penta-1,3-diene and buta-1,3-diene, a value of  $k_2 = 2.1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 480°C is obtained.



This is the first value determined for a reaction of this type and is at least ten times lower than rate constants for the formation of an alkene from an alkyl radical. This decrease is consistent with the considerably lower enthalpy change in reaction (2).

Product analysis suggests that H atoms add almost equally at the two positions in pent-2-ene, and in the ratio of  $0.65 \pm 0.2$  for non-terminal/terminal addition in pent-1-ene. In contrast to the behaviour of vibrationally-excited propyl and butyl radicals formed by H atom addition to alkenes, there is no evidence for an enhanced rate of decomposition of the pentyl radicals formed from the pentenes. Conjugate oxirans are formed mainly by  $HO_2$  addition to the pentenes, and lower aldehydes mainly by OH addition.

Studies of the separate addition of trace amounts of a number of alkanes to slowly reacting mixtures of  $H_2 + O_2$  at  $\approx 500^\circ\text{C}$  have given kinetic information on the reactions of H and OH radicals with the alkanes<sup>1</sup> and on the oxidation chemistry of the alkyl radicals formed in the primary attack.<sup>2-7</sup> Rate constants have been determined for the elementary steps involved in the oxidation of alkanes, and a near-quantitative interpretation in the initial stages of reaction is now possible.<sup>5-7</sup> However, for a full interpretation of the whole oxidation process at these temperatures it is necessary to consider the further oxidation of the products, such as conjugate alkenes which, in the early stages of reaction, are formed typically in yields of 50–98% at 400–500°C.<sup>3-8</sup> Unfortunately, the mechanism of alkene oxidation is not clear, and few kinetic data are available for the elementary reactions involved.

The gas-phase oxidation of alkenes other than ethylene and propene has been investigated only to a very limited extent, and this is particularly true for the pentenes. Hughes and Prodhan<sup>9</sup> examined pressure and temperature changes during the passage of cool flames through mixtures of each of the three isomeric pentenes with  $O_2$  with the initial temperature between 280 and 330°C, but made no analysis of the products. Cullis and Hirschler<sup>10</sup> made a partial examination of the products formed during the combustion of *n*-pentane in the presence of small quantities of isotopically-labelled pent-1-ene and pent-2-ene between 290 and 380°C. They showed that pentadienes were derived solely from the pentenes and

that the fraction of pentene converted into diene changed dramatically from  $\approx 30\%$  before the first cool flame to  $\approx 10\%$  just after. A striking feature was that prior to the cool flame, the fraction of pent-1-ene converted into penta-1,2-diene was approximately equal to the combined fractions of penta-1,3-diene and penta-1,4-diene.

The use of the  $H_2 + O_2$  system has been extended by addition of pent-1-ene and *cis*-pent-2-ene to complement the work with pentane,<sup>5</sup> where pentenes form  $\approx 50\%$  of the initial product and for which a successful interpretation of the initial products has been made.

## EXPERIMENTAL

The apparatus and general procedure have been described elsewhere.<sup>5,8</sup> Pent-1-ene and *cis*-pent-2-ene were supplied by Fluka A.G. with stated purities  $>99\%$ . The liquids were purified by trap-to-trap distillation under vacuum and degassed several times before use. After treatment, analysis by gas chromatography showed no impurity in either, except for a trace ( $<0.2\%$ ) of the *trans* isomer in the *cis*-pent-2-ene used. Gas chromatography was used for the analysis of all products except formaldehyde which was determined colorimetrically.<sup>11</sup>

## ANALYTICAL RESULTS

A full analysis of products was carried out for the mixture  $O_2 = 70$ ,  $H_2 = 140$ ,  $N_2 = 285$  Torr containing 5 Torr of either pent-1-ene or *cis*-pent-2-ene, and partial analyses have been carried out with mixtures of different oxygen content. A few minor peaks on the g.l.c. traces were not assigned. All appeared to be due to

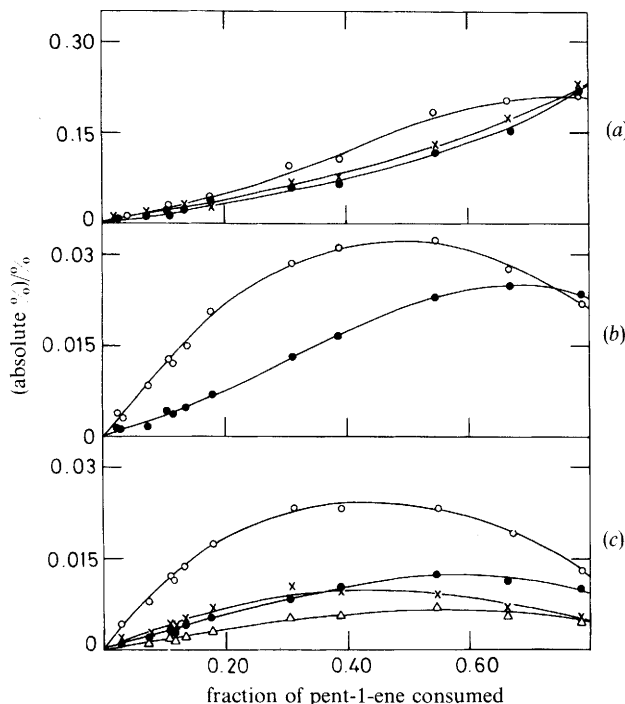


FIG. 1.—Variation of products with consumption of pent-1-ene.  $H_2 = 140$ ,  $O_2 = 70$ ,  $N_2 = 285$ , pent-1-ene = 5 Torr;  $480^\circ C$ . (a)  $\circ$ ,  $C_3H_6$ ;  $\times$ ,  $C_2H_4$ ;  $\bullet$ ,  $CH_4$ . (b)  $\circ$ , buta-1,3-diene;  $\bullet$ , but-1-ene. (c)  $\circ$ , *trans*-penta-1,3-diene;  $\times$ , *cis*-penta-1,3-diene;  $\bullet$ , *trans*-pent-2-ene;  $\Delta$ , *cis*-pent-2-ene.

secondary products and are not the concern of this paper. No analyses were made for  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , or  $\text{H}_2\text{O}_2$ .

Product profiles are shown in fig. 1 and 2 for pent-1-ene and in fig. 3 and 4 for *cis*-pent-2-ene, as a function of pentene consumed. All the products reported are formed in primary processes, although a number are additionally formed as secondary products. The initial yields of products at 5% consumption of pentene (expressed as the percentage of pentene consumed on a mole per mole basis) are given in table 1; reliable figures for the yields earlier in the reaction are not possible because of the rapid rate of oxidation of the pentenes. Because of this high reactivity, secondary processes will only become important at a later stage in the reaction. No penta-1,2-diene or penta-2,3-diene was found, although trace amounts of the 1,4-diene were detected. These observations contrast markedly with those of Cullis and Hirschler<sup>10</sup> who found that penta-1,2-diene was the major initial product prior to the first cool flame of pent-1-ene at 290–380°C. Two other features may be noted. (i) The relatively low yield of 2-methyl-3-ethyloxiran from pent-2-ene compared with the high yield of the equivalent oxiran, 2-propyloxiran, from pent-1-ene. (ii) The relatively large yields of 2,4-dimethyloxetan, 2-methyltetrahydrofuran, and tetrahydropyran in the present work. Cullis and Hirschler<sup>10</sup> suggest, from their radiochemical studies, that these compounds are not formed from the pentenes. This apparent discrepancy is simply resolved as the addition of H atoms, present in the  $\text{H}_2 + \text{O}_2$  system, gives rise to pentyl radicals which, *via* formation of peroxy radicals, will undergo peroxy radical isomerisation and decomposition reactions to form O-heterocyclic compounds as discussed later.

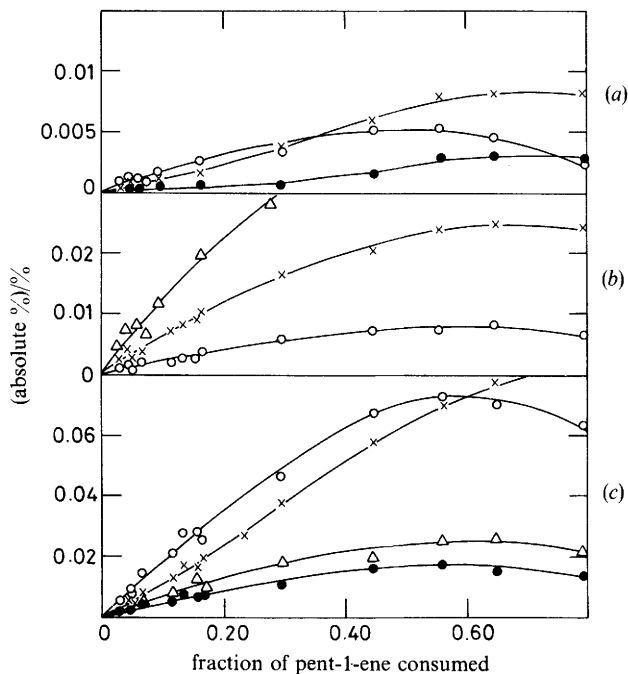


FIG. 2.—Variation of products with consumption of pent-1-ene.  $\text{H}_2 = 140$ ,  $\text{O}_2 = 70$ ,  $\text{N}_2 = 285$ , pent-1-ene = 5 Torr; 480°C. (a)  $\circ$ , 2-ethyloxetan;  $\times$ , propionaldehyde;  $\bullet$ , methylethylketone. (b)  $\Delta$ , HCHO;  $\times$ , 2,4-dimethyloxetan;  $\circ$ , tetrahydropyran. (c)  $\circ$ , 2-propyloxiran;  $\bullet$ , butyraldehyde;  $\Delta$ , 2-methyltetrahydrofuran;  $\times$ , acetaldehyde.

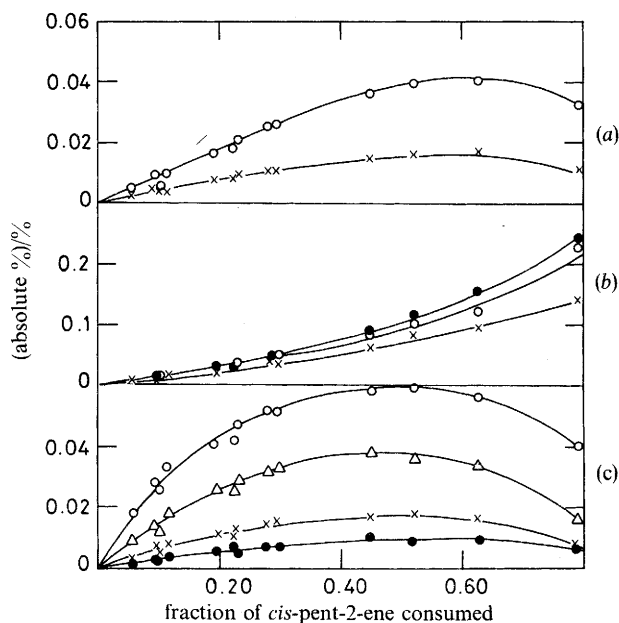


FIG. 3.—Variation of products with consumption of *cis*-pent-2-ene.  $H_2 = 140$ ,  $O_2 = 70$ ,  $N_2 = 285$ , *cis*-pent-2-ene = 5 Torr;  $480^\circ C$ . (a) O, but-1-ene; x, buta-1,3-diene. (b) ●,  $CH_4$ ; ○,  $C_2H_4$ ; x,  $C_3H_6$ . (c) ○, *trans*-pent-2-ene; Δ, *trans*-penta-1,3-diene; x, *cis*-penta-1,3-diene; ●, pent-1-ene.

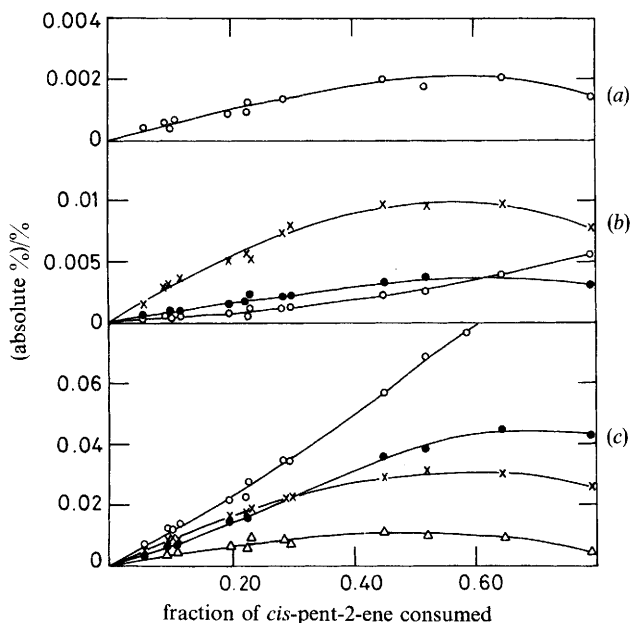


FIG. 4.—Variation of products with consumption of *cis*-pent-2-ene.  $H_2 = 140$ ,  $O_2 = 70$ ,  $N_2 = 285$ , *cis*-pent-2-ene = 5 Torr;  $480^\circ C$ . (a) O, butyraldehyde. (b) x, 2-methyl-3-ethyloxiran; ●, tetrahydropyran; ○, methylethylketone. (c) ○, acetaldehyde; x, 2,4-dimethylloxetan; ●, propionaldehyde; Δ, 2-methyltetrahydrofuran.

TABLE 1.—RELATIVE PERCENTAGE YIELDS OF PRODUCTS FROM PENT-1-ENE AND *cis*-PENT-2-ENE  
 $H_2 = 140$ ,  $O_2 = 70$ ,  $N_2 = 285$ , pentene = 5 Torr,  $480^\circ C$ , 5% consumption of pentene.

product	pent-1-ene	<i>cis</i> -pent-2-ene
pent-1-ene	—	2.2
<i>cis</i> -pent-2-ene	1.1	—
<i>trans</i> -pent-2-ene	2.5	30.5
<i>cis</i> -penta-1,3-diene	4.3	6.0
<i>trans</i> -penta-1,3-diene	11.0	14.7
2-propyloxiran	18.7	trace
2-methyl-3-ethyloxiran	trace	3.0
2-ethyloxetan	1.7	trace
2,4-dimethyloxetan	6.3	8.4
2-methyltetrahydrofuran	9.6	3.5
tetrahydropyran	2.3	0.8
but-2-ene	1.8	9.3
buta-1,3-diene	12.2	3.8
butyraldehyde	4.5	0.4
methylethylketone	0.5	0.3
propene	18.9	9.0
propionaldehyde	1.3	6.5
ethylene	18.0	11.0
acetaldehyde	10.3	9.8
methane	14.4	11.0
formaldehyde	13.5	7.5
carbon monoxide	9.1	5.7

## DISCUSSION

The extremely limited information available on the complex mechanism of alkene oxidation and on the rate constants of the elementary reactions involved will not allow a detailed interpretation of the formation of all the products detected. Attention is therefore confined to the major products and, in particular, to the relative importance of the different types of reaction, such as radical addition and abstraction.

The primary products may be conveniently divided into four groups, according to the proposed mechanism of formation from the pentenes. (a) By H atom abstraction: penta-1,3-diene, buta-1,3-diene,  $CH_4$  (partly), and formaldehyde (partly). (b) By H atom addition to give pentyl radicals: pentenes, but-1-ene, propene, ethylene,  $C_5$  O-heterocycles (except the major part of the oxirans), acetaldehyde (partly),  $CH_4$  (partly) and formaldehyde (partly). (c) By OH radical addition: butyraldehyde, propionaldehyde, acetaldehyde (partly) and formaldehyde (partly). (d) By  $HO_2$  radical addition: 2-propyloxiran and 2-methyl-3-ethyloxiran.

## H ATOM ABSTRACTION

H atom abstraction by the radicals O, H, OH and  $HO_2$  occurs most easily at the allylic positions in the pentenes because of the formation of resonance-stabilised pentenyl radicals. Table 2 lists the possible abstraction reactions, together with the

TABLE 2.—ABSTRACTION REACTIONS OF THE PENTENES

reaction	product	radical	$\Delta H/\text{kJ mol}^{-1}$		
			R = OH	R = H	R = HO <sub>2</sub> <sup>a</sup>
R + CH <sub>2</sub> =CHCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> CHCHCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	I	-147	-84	-25
	CH <sub>2</sub> =CHCH <sub>2</sub> CHCH <sub>3</sub>	II	-96	-33	26
	CH <sub>2</sub> =CHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	III	-78	-15	44
	CH <sub>2</sub> =CCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	IV	-68	-5	54
	CH=CHCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	V	-55	8	67
R + CH <sub>3</sub> CH=CHCH <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> CHCHCH <sub>2</sub> CH <sub>3</sub>	I	-139	-76	-17
	CH <sub>3</sub> CHCHCHCH <sub>3</sub>	VI	-147	-84	-25
	CH <sub>3</sub> CH=CHCH <sub>2</sub> CH <sub>2</sub>	VII	-78	-15	44
	CH <sub>3</sub> C=CHCH <sub>2</sub> CH <sub>3</sub>	VIII	-68	-5	54
	CH <sub>3</sub> CH=CCH <sub>2</sub> CH <sub>3</sub>	IX	-55	8	67

<sup>a</sup>  $D(\text{HOO}-\text{H}) = 377 \text{ kJ mol}^{-1}$ .

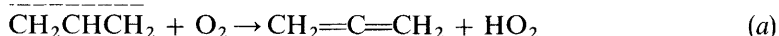
enthalpy changes. Although, because of the lack of data, the absolute values may only be accurate to  $\pm 15 \text{ kJ mol}^{-1}$ , it is the differences in the values that are important and these are much more reliable. The relative rate of formation of radicals IV and V from pent-1-ene and radicals VIII and IX from pent-2-ene through H and HO<sub>2</sub> attack will be extremely low, and even attack by the relatively unselective OH radical will produce very few of these radicals.<sup>1</sup> As previous studies<sup>1</sup> suggest that at least 50% of the abstraction will occur by H and HO<sub>2</sub> attack, particularly in the early stages where interpretation is attempted, it is almost certain that radicals IV, V, VIII and IX play a very minor role in the oxidation and they will not be considered further. Thus, with pent-1-ene the resonance-stabilised radical I will dominate, and with pent-2-ene the resonance-stabilised radicals I and VI will be even more dominant.

Pentadienes may be produced in a reaction of the pentenyl radicals with O<sub>2</sub> analogous to the formation of conjugate alkenes from alkyl radicals, and the various possibilities are listed in table 3 with the associated enthalpy changes which vary between  $-76$  and  $54 \text{ kJ mol}^{-1}$ . Studies with n-butane<sup>3</sup> have suggested that the conjugate alkene is either formed in the direct bimolecular reaction  $\text{R} + \text{O}_2$  or possibly *via* the RO<sub>2</sub> radical, but not from the QOOH radical formed from the RO<sub>2</sub> radical by H atom transfer. As under most conditions R and RO<sub>2</sub> are effectively equilibrated, the first two routes cannot be distinguished experimentally. On theoretical grounds the direct bimolecular process is preferred<sup>6</sup> and it will be assumed that the pentadienes are formed in this way.

Due to the large differences in enthalpy change in the two reactions of radical I and of VI, negligible quantities of penta-1,2-diene and penta-2,3-diene should be formed. Although formation of penta-1,4-diene from radical II is slightly more favourable and radical III may solely give this diene, very low yields are to be expected because radicals II and III will only be formed to a slight extent by H abstraction as shown by the enthalpy changes in table 2. Consequently, the observation that, apart from a trace of penta-1,4-diene, the only pentadiene found is the 1,3 isomer is entirely consistent with the thermochemistry of the reactions involved.

As the effects of the differences in the enthalpy change will be even greater at the lower temperatures used by Cullis and Hirschler,<sup>10</sup> the proportion of 1,2- and 2,3-dienes should be even lower than in the present work. The very high yields of

these dienes at their temperatures are completely inconsistent with the thermochemistry involved, and the likeliest explanation is that the 1,2- and 2,3-dienes are formed in surface processes. The observation that their relative yield reaches a sharp maximum just before the first cool flame could be explained by a surface process which is rapidly swamped by an autocatalytic homogeneous oxidation as the cool flame is generated. A similar effect has been observed with the surface formation of CO<sub>2</sub> in the oxidation of propionaldehyde.<sup>12</sup> The absence of the 1,2- and 2,3-pentadienes in the present work is also consistent with the absence of allene from the products when propene is added to slowly reacting mixtures of H<sub>2</sub> + O<sub>2</sub> at 480°C,<sup>13</sup> which suggests that reaction (a) cannot compete with alternative reactions of the allyl radical. Similarly, no buta-1,2-diene is observed when but-1-ene and but-2-ene are used as additives.<sup>3</sup>



Buta-1,3-diene is formed from both pentenes, the simplest route being the decomposition of radical I.



Three pieces of evidence provide support for this: (i) The high yields of methane, presumably formed by the reaction of CH<sub>3</sub> radicals with H<sub>2</sub>, from pent-1-ene cannot be accounted for unless reaction (1) is virtually the sole source of buta-1,3-diene. Studies of the addition of alkanes<sup>2-4</sup> to slowly reacting mixtures of H<sub>2</sub> + O<sub>2</sub> at 480°C have shown that 75% of CH<sub>3</sub> radicals react with H<sub>2</sub> to form methane with the mixture containing 70 Torr of O<sub>2</sub>. (ii) The initial value of the ratio [penta-1,3-diene]/[buta-1,3-diene] for pent-1-ene increases from 1.25 to 5.5 as the pressure of O<sub>2</sub> is increased from 70 to 355 Torr. (iii) With pentane as additive, the relative yield of buta-1,3-diene, which is formed as a secondary product, increases markedly as the O<sub>2</sub> pressure is reduced from 70 to 8 Torr.<sup>5</sup>

Comment (i) precludes the formation of buta-1,3-diene from radical III by a peroxy radical isomerisation and decomposition sequence because no methane would be formed, and other sources of CH<sub>4</sub> are insufficient to give a yield of 14%.

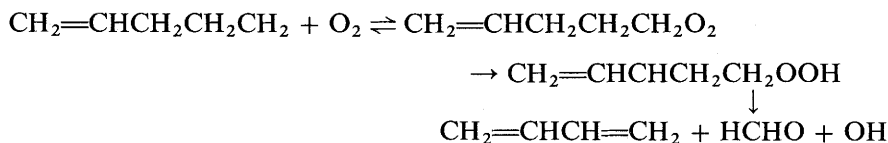


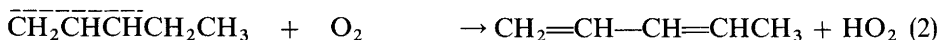
TABLE 3.—FORMATION OF PENTADIENES

radical	reaction	$\Delta H/$ kJ mol <sup>-1</sup>
I	$\text{CH}_2\text{CHCHCH}_2\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_2=\text{C}=\text{CHCH}_2\text{CH}_3 + \text{HO}_2$	54
	$\rightarrow \text{CH}_2=\text{CHCH}=\text{CHCH}_3 + \text{HO}_2$	-14
II	$\text{CH}_2=\text{CHCH}_2\text{CHCH}_3 + \text{O}_2 \rightarrow \text{CH}_2=\text{CHCH}=\text{CHCH}_3 + \text{HO}_2$	-65
	$\rightarrow \text{CH}_2=\text{CHCH}_2\text{CH}=\text{CH}_2 + \text{HO}_2$	-37
III	$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2 + \text{O}_2 \rightarrow \text{CH}_2=\text{CHCH}_2\text{CH}=\text{CH}_2 + \text{HO}_2$	-55
VI	$\text{CH}_3\text{CHCHCHCH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{CH}=\text{C}=\text{CHCH}_3 + \text{HO}_2$	54
	$\rightarrow \text{CH}_2=\text{CHCH}=\text{CHCH}_3 + \text{HO}_2$	-7
VII	$\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{CH}=\text{CHCH}=\text{CH}_2 + \text{HO}_2$	-76

Further, it is extremely unlikely that radical III is formed in sufficient quantity to account for the relatively high yield of buta-1,3-diene.

The dependence of the [penta-1,3-diene]/[buta-1,3-diene] ratio on the O<sub>2</sub> pressure also suggests that the major part of the penta-1,3-diene is formed *via* radical I, which is consistent with the view that on thermochemical grounds (table 2) radical II will be formed in smaller amounts than I. If the two dienes are formed solely from radical I, then their relative rate of formation is given by eqn (i).

$$d[\text{penta-1,3-diene}]/d[\text{buta-1,3-diene}] = k_2[\text{O}_2]/k_1 \quad (\text{i})$$



Thus the initial value of the product ratio should increase by a factor of 5.07 when the pressure of O<sub>2</sub> is increased from 70 to 355 Torr, compared with the observed increase of 4.4. Even allowing for experimental error, the difference in the two values of the increase is probably significant, and could be explained if a small amount of penta-1,3-diene is formed from radical II. The product analysis provides no evidence that products other than dienes are formed from pentenyl radicals, and accepting that radical II uniquely gives penta-1,3-diene, then the difference between the experimental change in the product ratio with increase in O<sub>2</sub> pressure and that predicted by eqn (i) suggests that the relative rate of formation of radicals I and II is 5.0. With this ratio, then for pent-1-ene 70% of the penta-1,3-diene is formed from radical I with O<sub>2</sub> = 70 Torr and 80% with O<sub>2</sub> = 355 Torr, and use of eqn (i) gives the value  $k_2/k_1 = 590 \text{ dm}^3 \text{ mol}^{-1}$  at 480°C.

No independent value of  $k_1$  or  $k_2$  is available, but an estimate of  $k_2$ , accurate to a factor of  $\approx 2$ , may be obtained by use of the data of Cvetanovic and Irwin<sup>14</sup> for

TABLE 4.—RATE CONSTANTS FOR THE FORMATION OF ALKENES AT 480°C

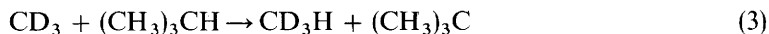
reaction	product	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (per C—H bond)	$\Delta H/\text{kJ mol}^{-1}$	ref., note
<i>primary C—H</i>					
$\overline{\text{CH}_3\text{CH}_2} + \text{O}_2$	C <sub>2</sub> H <sub>4</sub>	$6.6 \times 10^7$	$2.2 \times 10^7$	-45	a,b
$\overline{\text{CH}_3\text{CHCH}_3} + \text{O}_2$	C <sub>3</sub> H <sub>6</sub>	$1.27 \times 10^8$	$2.1 \times 10^7$	-39.5	c
$\overline{\text{CH}_2\text{CHCH}_2\text{CH}_3} + \text{O}_2$	C <sub>4</sub> H <sub>8</sub> - 1	$5.1 \times 10^7$	$1.7 \times 10^7$	-37.5	3
<i>secondary C—H</i>					
$\overline{\text{CH}_3\text{CH}_2\text{CH}_2}$	C <sub>3</sub> H <sub>6</sub>	$7.1 \times 10^7$	$3.6 \times 10^7$	-53.5	d
$\overline{\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2}$	C <sub>4</sub> H <sub>8</sub> - 1	$1.6 \times 10^8$	$8 \times 10^7$	-55.5	3
$\overline{\text{CH}_3\text{CHCH}_2\text{CH}_3}$	<i>trans</i> -C <sub>4</sub> H <sub>8</sub> - 2	$7.8 \times 10^7$	$3.9 \times 10^7$	-49	3
	<i>cis</i> -C <sub>4</sub> H <sub>8</sub> - 2	$4.3 \times 10^7$	$2.2 \times 10^7$	-45	3
<i>tertiary C—H</i>					
$(\text{CH}_3)_2\overline{\text{CHCH}_2}$	<i>i</i> -C <sub>4</sub> H <sub>8</sub>	$6.8 \times 10^7$	$6.8 \times 10^7$	-61.5	4
<i>allyl C—H</i>					
$\overline{\text{CH}_2\text{CHCH}_2\text{CH}_3}$	CH <sub>2</sub> =CHCH=CHCH <sub>3</sub>	$2.1 \times 10^6$	$1.05 \times 10^6$	-14	present work

<sup>a</sup> R. R. Baldwin, D. H. Langford and R. W. Walker, *Trans. Faraday Soc.*, 1969, **65**, 792; 806.

<sup>b</sup> Calculated from  $k(\text{overall}) = 5.5 \times 10^7$  at 440°C, with  $E = 21 \text{ kJ mol}^{-1}$ . <sup>c</sup> R. R. Baldwin, C. J. Cleugh and R. W. Walker, *J.C.S. Faraday I*, 1976, **72**, 1715. <sup>d</sup> R. R. Baker, R. R. Baldwin and R. W. Walker, *Trans. Faraday Soc.*, 1970, **66**, 3016.



reaction (-1). Over the temperature range 80–180°C they give  $E_3 - E_{-1} = 14.5 \text{ kJ mol}^{-1}$  and  $A_{-1}/A_3 = 2.4$ . On the reasonable assumption that  $\text{CH}_3$  and  $\text{CD}_3$  radicals abstract from isobutane at virtually the same rate, these parameters may be combined with  $k_3 = 10^{8.47} e^{-4130/T} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  given by Jackson *et al.*<sup>15</sup> for the range 300–460°C to obtain  $k_{-1} = 3.0 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 480°C.



Use of thermochemical additivity data<sup>16</sup> gives  $K_{-1} = 8350 \text{ dm}^3 \text{ mol}^{-1}$ , so that  $k_1 = 3.6 \times 10^3 \text{ s}^{-1}$ ; from  $k_2/k_1 = 590 \text{ dm}^3 \text{ mol}^{-1}$ ,  $k_2 = 2.1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 480°C. This is the first value of a rate constant obtained for the formation of a conjugate diene from the reaction of an alkenyl radical with  $\text{O}_2$  and, as shown in table 4, it is considerably below the values for the corresponding reaction of alkyl radicals. However, as table 4 also shows, the alkenes are formed in reactions which are 24–28  $\text{kJ mol}^{-1}$  more exothermic than reaction (2) of the pentenyl radical. Expressed on a per C—H bond basis, there is a clear trend for the rate constant to increase with increase in exothermicity. A simple relation between the two quantities may be developed by assuming that the rate constant is given by the Arrhenius expression  $k = Ae^{-E/RT}$ , that  $A$  (per C—H bond) is constant for all reactions in table 4 and that the Evans–Polanyi relationship  $E = a + b\Delta H$  holds, where  $a$  and  $b$  are constants. At a particular temperature,  $\log_e k$  is then given by expression (ii).

$$\log_e k = \log_e A - a/RT - b\Delta H/RT = A' - b\Delta H/RT \quad (\text{ii})$$

Fig. 5 shows that a straight line relationship is obtained when  $\log_{10} k$  is plotted against  $\Delta H$  for the data in table 4. Use of the empirical relationship (iii), where  $\Delta H$  is in  $\text{kJ mol}^{-1}$ , predicts the values of the rate constants to better than a factor of 1.4.

$$\log_{10} k = 5.50 - 0.0411 \Delta H \quad (\text{iii})$$

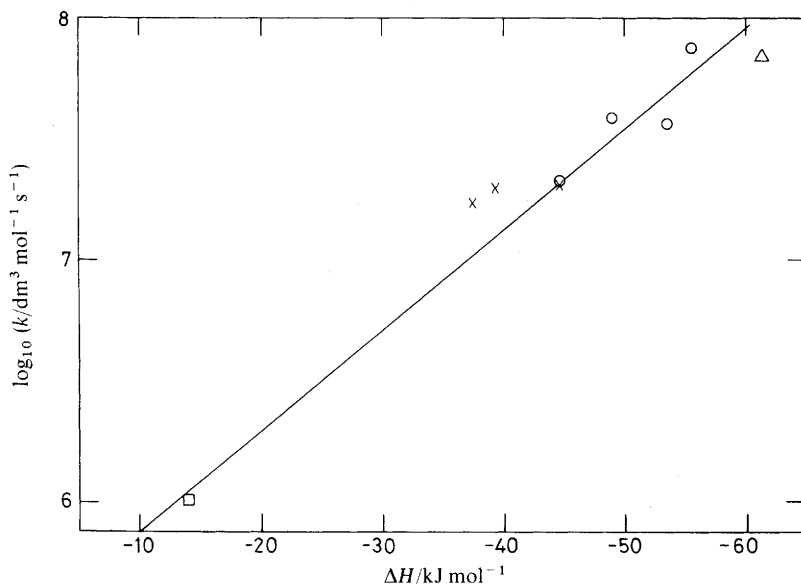
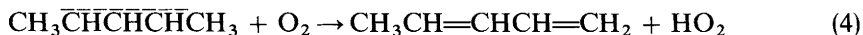


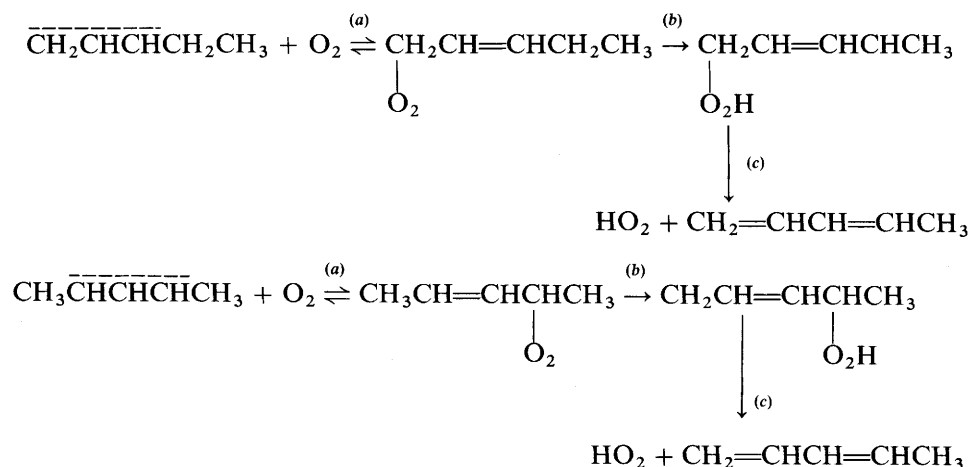
FIG. 5.—Plot of  $\log_{10} k$  (per C—H bond) against  $\Delta H$  for the formation of alkenes at 480°C.  $\Delta$ , tertiary C—H;  $\circ$ , secondary C—H;  $\times$ , primary C—H;  $\square$ , allyl C—H.

The relationship between activation energy and enthalpy change for reactions of radicals with alkanes<sup>17</sup> suggests that the plot of  $\log_{10}k$  against  $\Delta H$  should show a continuous curve with a slope approaching zero at high negative values of  $\Delta H$  ( $\Delta H \approx -100 \text{ kJ mol}^{-1}$ ) and approaching  $1/2.303RT = 0.070 \text{ mol kJ}^{-1}$  (i.e.  $b = 1$ ) when the reaction is highly endothermic ( $\Delta H > 100 \text{ kJ mol}^{-1}$ ). Thus, use of the average slope of fig. 5 gives an upper limit of  $10^{3.3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at  $480^\circ\text{C}$  for the rate constants for the formation of penta-1,2-diene and penta-2,3-diene from radicals I and VI, respectively. This value may be compared with  $k_2 = 2.1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $k_4 = 6.1 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  (see below), thus confirming that negligible amounts of these dienes should be formed in the present work.



For the mixture containing 70 Torr of  $\text{O}_2$ , the initial value of the ratio [penta-1,3-diene]/[buta-1,3-diene] increases from 1.25 with pent-1-ene to 5.4 with pent-2-ene. This increase may be attributed to the additional formation of penta-1,3-diene from radical VI and to a minor extent from VII, whereas radical I is still the sole source of buta-1,3-diene. Accepting that pentenyl radicals react only to give dienes, then the product yields suggest that the relative rate of formation of radicals VI and I from pent-1-ene is 2.4 for the mixture containing 70 Torr of  $\text{O}_2$ , in general agreement with the thermochemistry involved. The results for pent-2-ene cannot be used to determine a rate constant  $k_4$  for the formation of penta-1,3-diene from radical VI but, by use of the  $\Delta H$  value in table 4, eqn (iii) suggests  $k_4 = 6.1 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at  $480^\circ\text{C}$ .

There is no evidence from the product distribution to suggest that the peroxy radical isomerisation and decomposition (PRID) sequence, so important in the formation of O-ring compounds from alkyl radicals,<sup>6</sup> contributes to the removal of the resonance-stabilised pentenyl radicals I and VI. However, from a consideration of the elementary steps involved, it is not possible to exclude the possibility that the PRID sequence is important in the formation of the pentadienes as follows.

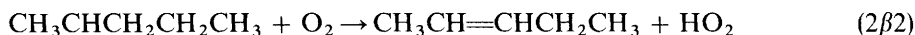
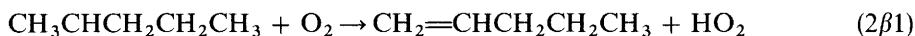
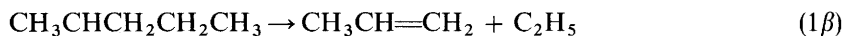


Although it has been shown<sup>3</sup> that the PRID sequence is not responsible for the formation of conjugate alkene from alkyl radicals at  $\approx 500^\circ\text{C}$ , the rate constants for the elementary processes involved differ considerably for the cases of alkyl radicals and resonance-stabilised pentenyl radicals. Whereas  $K_a \approx 1 \text{ dm}^3 \text{ mol}^{-1}$  for radicals

I and VI compared with values of  $10^2 - 10^3$  at  $480^\circ\text{C}$  for alkyl radicals,  $k_b$  may be considerably higher than for alkyl radicals because, first, attack at the weak allylic position will occur, and secondly, in contrast to alkylperoxy radicals where only the highly strained 1,4 isomerisations lead to alkenes, with radicals I and VI 1,6 and 1,5 isomerisations, respectively, will give the pentadienes. A final decision on the precise route of formation of the diene must await further experimental evidence.

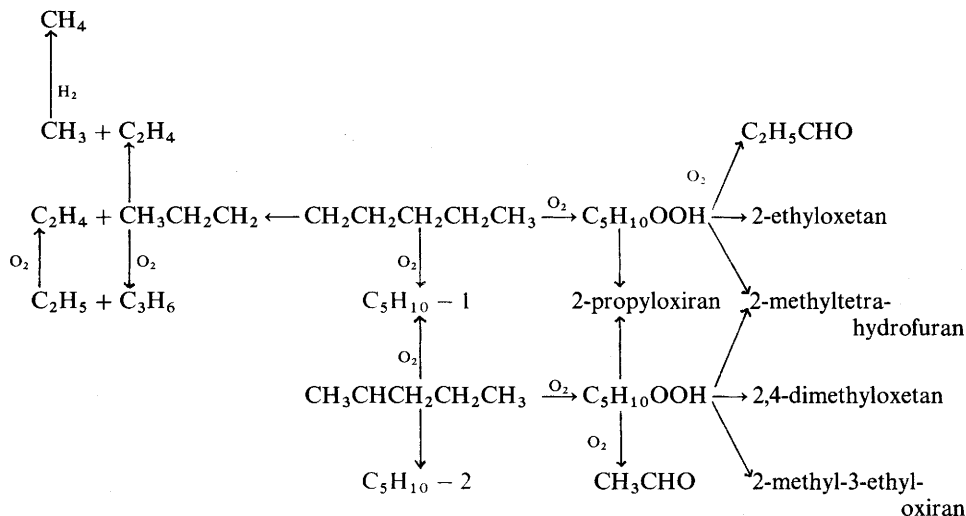
#### H ATOM ADDITION TO GIVE PENTYL RADICALS

2,4-dimethyloxetan (2,4-DMO), 2-methyltetrahydrofuran (2-MTHF), tetrahydropyran (THP), pent-2-ene (from pent-1-ene), and pent-1-ene and *trans*-pent-2-ene (from *cis*-pent-2-ene) almost certainly arise solely from pentyl radicals formed by H atom addition to the pentenes. Schemes 1 and 2 show the proposed outline mechanisms for the formation of the products from the pentyl radicals for pent-1-ene and pent-2-ene, respectively. As the enthalpy change in the addition is  $\approx 150 \text{ kJ mol}^{-1}$ , the resultant pentyl radicals may be vibrationally excited and react differently from thermal pentyl radicals produced from pentane by H abstraction. In particular, the excited pentyl radicals may decompose to give propene, ethylene and but-1-ene at a considerably faster rate than their thermalised analogues, as was found with the excited radicals formed when but-1-ene,<sup>3</sup> but-2-ene,<sup>3</sup> isobutene,<sup>4</sup> and propene<sup>13</sup> were used as additives under the present conditions. However, the results with *cis*-pent-2-ene suggest that the rate of decomposition of the "excited" radicals is not noticeably increased relative to that of other reactions. According to the mechanism in Scheme 2, pent-1-ene and propene are only formed from the 2-pentyl radical in reactions  $(2\beta_1)^*$  and  $(1\beta)$ , respectively, and for the mixture with  $\text{O}_2 = 70 \text{ Torr}$  the initial value of  $[\text{propene}]/[\text{pentene-1}] = 4.0$ , compared with a calculated value of 3.1 using rate constants of  $k_{1\beta} = 2.3 \times 10^5 \text{ s}^{-1}$  and  $k_{2\beta_1} = 5.1 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  obtained from studies with pentane.<sup>5</sup> But-1-ene is only formed from the 3-pentyl radical, and use<sup>3,5</sup> of the rate constant ratio  $k_{2\beta_2(\text{trans})}/k_{2\beta_1} = 1.5$  with the yield of pent-1-ene allows the calculation of the yield of *trans*-pent-2-ene from the 2-pentyl radical, which corresponds to  $\approx 10\%$  of the total yield. Thus  $[\text{trans-pent-2-ene}]_3/[\text{but-1-ene}] = 2.9$ , compared with a value of 2.5 from the pentane studies.<sup>3</sup> There is, therefore, little evidence for an enhanced rate of decomposition of pentyl radicals formed from pentene by H atom addition. This is consistent with the observation that whereas all the vibrationally excited  $n\text{-C}_3\text{H}_7$  radicals formed by H atom addition to propene at  $480^\circ\text{C}$  appear to decompose,<sup>13</sup> 40–60% of the butyl radicals from but-1-ene and but-2-ene appear to be stabilised<sup>13</sup> under the same conditions.



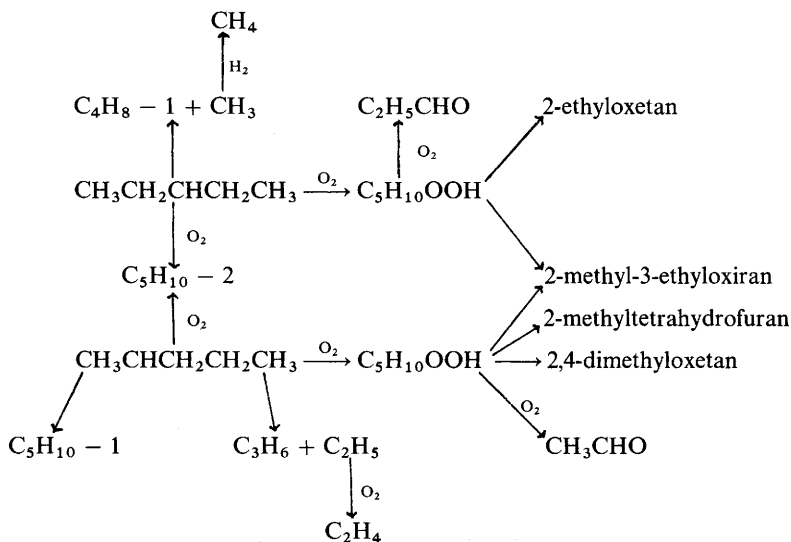
As the pentyl radicals formed by H atom addition to the pentenes appear to behave "normally", it should be possible to predict the relative amounts of the products formed from these radicals based on the schemes in schemes 1 and 2 and then make a comparison with the experimental results. The rate constants used are those determined for the various reactions from the pentane addition studies.<sup>5</sup> For

\* The reaction numbers used for the pentyl radicals are consistent with those used in a previous publication.<sup>5</sup>



SCHEME 1.—Outline mechanism for the formation of products from pentyl radicals (pent-1-ene).

*cis*-pent-2-ene, the yields of products from 3-pentyl radicals are calculated relative to the yield of but-1-ene, and for the 2-pentyl radical relative to that of propene. For pent-1-ene, the products from 1-pentyl are calculated relative to the yield of THP, and those from the 2-pentyl radical are again relative to that of propene. For *cis*-pent-2-ene, the agreement between the predicted and observed relative yields shown in table 5 is quite good, particularly in view of the relatively low yields of some of the products. With pent-1-ene, the agreement in table 6 is less satisfactory, probably due to the necessity of measuring the yields of products from the 1-pentyl radical relative to that of THP, which is present in very small amounts and difficult to measure precisely in the initial stages of reaction. The considerably higher yield



SCHEME 2.—Outline mechanism for the formation of products from pentyl radicals (*cis*-pent-2-ene).

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TABLE 5.—OBSERVED AND PREDICTED RELATIVE YIELDS OF PRODUCTS FROM *cis*-PENT-2-ENE *via* 2-PENTYL AND 3-PENTYL RADICALSO<sub>2</sub> = 70, H<sub>2</sub> = 140, N<sub>2</sub> = 285, *cis*-pent-2-ene = 5 Torr, 480°C, 5% consumption.

products	relative predicted yield/%			observed yield/%
	3-pentyl	2-pentyl	total	
but-1-ene <sup>a</sup>	9.3	—	9.3	9.3
2-ethyloxetan	0.50	—	0.50	trace
2-methyl-3-ethyloxiran <sup>b</sup>	0.67	0.90	1.57	3.0
<i>trans</i> -pent-2-ene	14.9	4.8	19.7	30.5
propene <sup>c</sup>	—	9.0	9.0	9.0
2-methyltetrahydrofuran	—	2.8	2.8	3.2
pent-1-ene	—	3.0	3.0	2.2
2,4-dimethyloxetan	—	7.4	7.4	8.4
acetaldehyde <sup>b</sup>	—	7.3	7.3	9.8

<sup>a</sup> Products from 3-P radicals calculated relative to the observed yield of but-1-ene. <sup>b</sup> Additional routes proposed for the formation of these compounds. <sup>c</sup> Products from 2-P radicals calculated relative to the observed yield of propene.

of 2-propyloxiran from pent-1-ene and of 2-methyl-3-ethyloxiran from pent-2-ene observed over the predicted yields almost certainly arises from the reaction of HO<sub>2</sub> radicals with the pentenes, as discussed later. The general agreement in tables 5 and 6 provides further support for the rate constants determined previously<sup>5</sup> for the reactions of the pentyl radicals, and indicates that the pentyl radicals formed by H atom addition to the pentenes react “normally” under the present conditions.

Use of the observed yields of products permits determination of the rate constant ratio for the addition of H atoms at the two positions in the pentenes. Where a product is formed from both adducts (see schemes 1 and 2), use of the rate constants for the elementary reactions involved allows the proportion of the product formed from each radical to be calculated. With *cis*-pent-2-ene, the major products are formed either completely or mainly from one of the two radicals, so that

TABLE 6.—OBSERVED AND PREDICTED RELATIVE YIELDS OF PRODUCTS FROM PENT-1-ENE FORMED *via* 1-PENTYL AND 2-PENTYL RADICALS

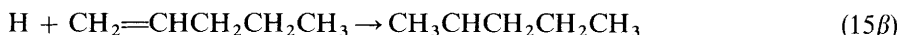
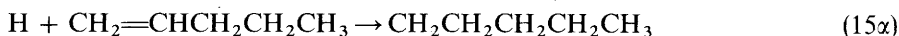
products	relative predicted yield/%			observed yield/%
	1-pentyl	2-pentyl	total	
tetrahydropyran <sup>a</sup>	2.3	—	2.3	2.3
ethyloxetan	3.7	—	3.7	1.7
2-propyloxiran <sup>b</sup>	0.55	0.05	0.60	18.7
2-methyltetrahydrofuran	16.5	1.1	17.6	9.6
propene	4.1	13.5	17.6	18.9
pentene-2 <sup>c</sup>	—	3.6	3.6	3.6
2-methyl-3-ethyloxiran	—	0.45	0.45	trace
2,4-dimethyloxetan	—	5.4	5.4	6.3
acetaldehyde	—	5.4	5.4	10.3

<sup>a</sup> Products from the 1-pentyl radical calculated relative to the observed yield of tetrahydropyran. <sup>b</sup> An additional route is proposed for the formation of this compound. <sup>c</sup> Products from the 2-pentyl radical calculated relative to the observed yield of pent-2-ene.

$k_{14\gamma}/k_{14\beta}$  may be determined reliably giving a value of  $1.3 \pm 0.2$ .



With pent-1-ene, the calculation is less reliable, and a value of  $k_{15\alpha}/k_{15\beta} = 0.65 \pm 0.2$  is obtained.

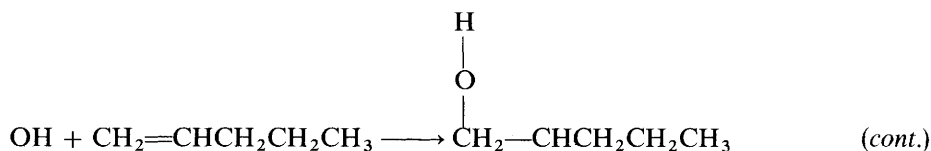


Falconer and Sunder<sup>18</sup> found 5.7% non-terminal addition of H atoms to propene at 298 K, but did not measure any temperature dependence. Kerr and Parsonage<sup>19</sup> have assumed equal A factors and used the results of Falconer and Sunder to suggest that the activation energy for non-terminal (nt) addition in propene is  $7.1 \text{ kJ mol}^{-1}$  higher than that for terminal (t) addition. On this basis,  $k_{nt}/k_t$  is 0.35 for propene at  $480^\circ\text{C}$ , but the uncertainty here must be at least  $\pm 0.2$ . Recently, Canosa and Marshall<sup>20</sup> have shown experimentally that the ratio  $k_{nt}/k_t$  for the addition of H atoms to isobutene does increase significantly with temperature, and over the range  $20\text{--}328^\circ\text{C}$  give  $\log_{10}(k_{nt}/k_t) = 0.47 \pm 0.33 - (16.6 \pm 2.6 \text{ kJ mol}^{-1} / 2.3RT)$ , so that  $k_{nt}/k_t$  (isobutene) =  $0.21 \pm 0.09$  at  $480^\circ\text{C}$ . The values of  $k_{nt}/k_t$  for isobutene and propene at  $480^\circ\text{C}$  are slightly below the value of  $k_{15\alpha}/k_{15\beta} = 0.65 \pm 0.2$  for pent-1-ene, although the uncertainties in the values for propene and pent-1-ene are sufficiently large for them to be indistinguishable. A value for isobutene lower than the other two is acceptable because the branched structure will lead to a larger difference in the activation energies for the non-terminal and terminal additions. Further discussion must await more experimental work, but there is little doubt that the discrimination in favour of terminal addition is much reduced as the temperature is increased from 25 to  $500^\circ\text{C}$ .

No other value of  $k_{14\gamma}/k_{14\beta}$  is available; a value close to unity is to be expected as non-terminal addition is involved in both cases.

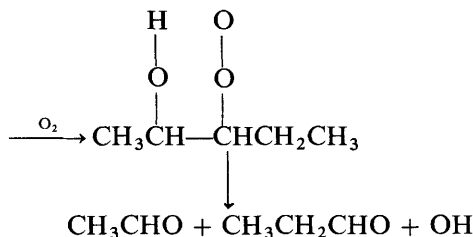
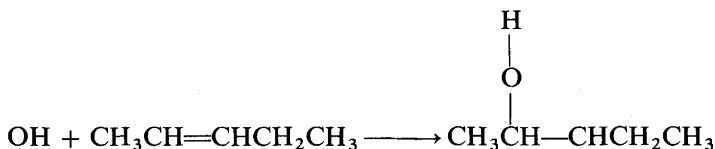
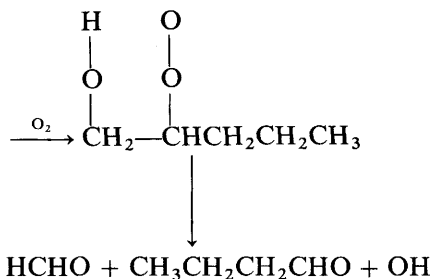
#### OH RADICAL ADDITION

Butyraldehyde is formed in significantly higher yield from pent-1-ene than from *cis*-pent-2-ene, whereas the reverse is true for propionaldehyde. This is consistent with the view expressed by Ray and Waddington<sup>21</sup> that lower aldehydes are formed by the sequential addition of OH\* radicals and O<sub>2</sub>, followed by decomposition.

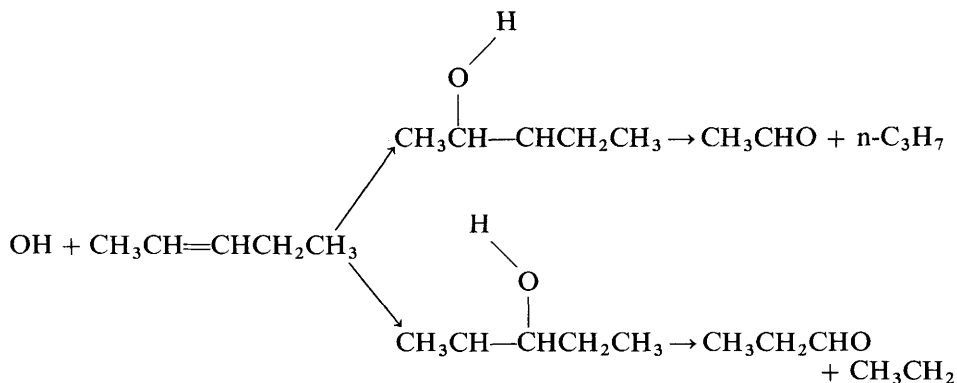


\* Addition of the OH radical to the alternative carbon atom leads to the same products.

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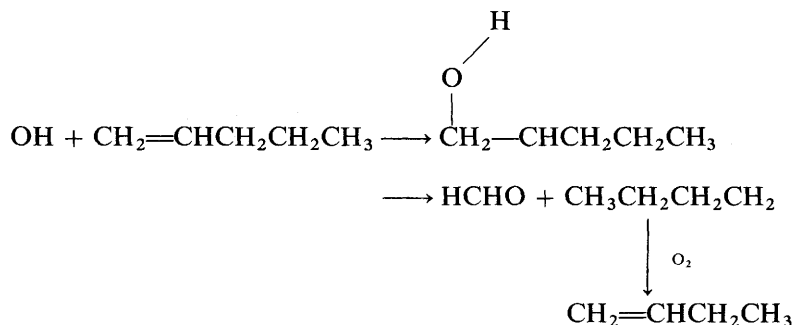


It has also been suggested<sup>22</sup> that OH addition alone may give aldehydes. Thus with pent-2-ene, OH addition could give two different sets of products.



If propionaldehyde and acetaldehyde were formed solely by the Waddington route, then [propionaldehyde] = [acetaldehyde] in the products from *cis*-pent-2-ene. Acetaldehyde is also formed as an alternative product to 2,4-dimethyloxetan (fig. 6 and 7). Allowing for this, the yield of acetaldehyde from OH addition is  $\approx 1.6\%$  compared with the 6.5% yield of propionaldehyde. The difference is just sufficient to suggest that both types of OH addition occur, and this is supported by the noticeable amount of but-1-ene formed from pent-1-ene, which cannot arise from the simple decomposition of a pentyl radical as is the case with formation from pent-2-

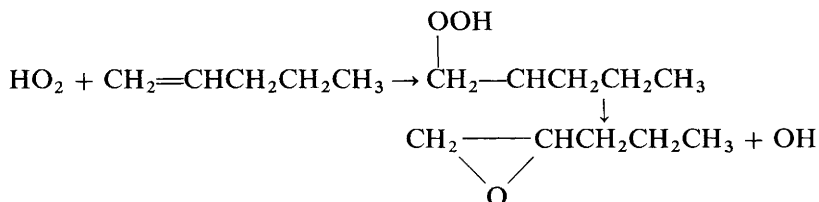
ene. The most obvious route for the formation of the but-1-ene involves the addition of OH to pent-1-ene as follows.



Insufficient data are available at present to enable these proposed mechanisms to be tested kinetically.

### HO<sub>2</sub> RADICAL ADDITION

Of the total yield of 2-propyloxiran of 18.7% from pent-1-ene, only ≈0.6% may be attributed to the PRID rearrangements of the 1-pentyl and 2-pentyl radicals formed by H atom addition to the alkene, discussed earlier. Almost certainly, the major source of the oxiran is HO<sub>2</sub> addition to the double bond followed by loss of an OH radical.



In contrast, most of the 2-methyl-3-ethyloxiran from pent-2-ene appears to arise from a PRID mechanism involving pentyl radicals and very little *via* HO<sub>2</sub> addition to the double bond. Several plausible explanations of this may be advanced, but there are insufficient experimental data to proceed further.

<sup>1</sup> R. R. Baldwin and R. W. Walker, *J.C.S. Faraday I*, 1979, **75**, 140.

<sup>2</sup> R. R. Baker, R. R. Baldwin, C. J. Everett and R. W. Walker, *Combustion and Flame*, 1975, **25**, 285.

<sup>3</sup> R. R. Baker, R. R. Baldwin, A. R. Fuller and R. W. Walker, *J.C.S. Faraday I*, 1975, **71**, 736; 756.

<sup>4</sup> R. R. Baker, R. R. Baldwin and R. W. Walker, *J.C.S. Faraday I*, 1978, **74**, 2229.

<sup>5</sup> R. R. Baldwin, J. P. Bennett and R. W. Walker, *J.C.S. Faraday I*, 1980, **76**, 1075.

<sup>6</sup> R. W. Walker, *Reaction Kinetics* (Spec. Period. Rep., The Chemical Society, London, 1975), vol. 1, p. 161.

<sup>7</sup> R. R. Baldwin, J. P. Bennett and R. W. Walker, *16th Int. Combustion Symp.*, (Combustion Institute, Pittsburgh, 1977), p. 1041.

<sup>8</sup> R. R. Baldwin, D. E. Hopkins and R. W. Walker, *Trans. Faraday Soc.*, 1970, **66**, 189.

<sup>9</sup> R. Hughes and A. S. Prodhan, *Combustion and Flame*, 1973, **20**, 297.

<sup>10</sup> C. F. Cullis and M. M. Hirschler, *Proc. Roy. Soc. A*, 1978, **364**, 75; 309.

<sup>11</sup> C. E. Bricker and H. R. Johnson, *Ind. and Eng. Chem. (Anal.)*, 1945, **19**, 400.

<sup>12</sup> R. R. Baldwin, K. A. Lewis and R. W. Walker, *Combustion and Flame*, 1979, **34**, 275.

<sup>13</sup> R. R. Baldwin, B. Tunnicliffe and R. W. Walker, unpublished work.

<sup>14</sup> R. J. Cvetanovic and R. S. Irwin, *J. Chem. Phys.*, 1967, **46**, 1694.



## 2412 PENTENE ADDITION TO HYDROGEN + OXYGEN REACTION

- <sup>15</sup>W. M. Jackson, J. R. McNesby and B. de B. Darwent, *J. Chem. Phys.*, 1962, **37**, 1610.  
<sup>16</sup>S. W. Benson, *Thermochemical Kinetics* (Wiley-Interscience, New York, 1976).  
<sup>17</sup>R. R. Baldwin and R. W. Walker, *J.C.S. Perkin II*, 1973, 361.  
<sup>18</sup>W. E. Falconer and W. A. Sunder, *Int. J. Chem. Kinetics*, 1971, **3**, 395.  
<sup>19</sup>J. A. Kerr and M. J. Parsonage, *Evaluated Kinetic Data on Gas Phase Addition Reactions* (Butterworths, London, 1972).  
<sup>20</sup>C. E. Canosa and R. M. Marshall, *J.C.S. Faraday I*, 1980, **76**, 846.  
<sup>21</sup>D. J. M. Ray and D. J. Waddington, *Combustion and Flame*, 1973, **20**, 327.  
<sup>22</sup>R. R. Baldwin, C. J. Everett, D. E. Hopkins and R. W. Walker, *Adv. Chem. Series*, no. 76, 1968, p. 124.

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