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Addition of 2,2,3-Trimethylbutane to Slowly Reacting Mixtures of Hydrogen and Oxygen at 480 °C

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The oxidation of 2,2,3-trimethylbutane (TRIMB) has been studied by adding traces of the alkane to slowly reacting mixtures of $H_2 + O_2$ in aged boric-acid-coated vessels at 480 °C. Rate constants for H and OH attack on TRIMB have been obtained and, by use of an additivity principle, Arrhenius parameters of $\log_{10} (A/dm^3 mol^{-1} s^{-1}) = 9.32 \pm 0.13$ and $E = 460 \pm 950 \text{ J mol}^{-1}$ are suggested for OH attack at a tertiary C—H bond in alkanes from a combination of the present results with studies at lower temperatures.

Propene, isobutene, and 2,2,3-trimethylbut-1-ene (TRIMB-1) are the major initial products, the yield of the latter increasing markedly at high O_2 pressures. The proportions of the three species of trimethylbutyl radicals formed in each mixture have been estimated. Two of the species of trimethylbutyl radicals react almost completely by homolysis of the strained central C—C bond to give propene and isobutene as products. The third radical $(CH_2)_2 CC(CH_3)_2$ is removed by either reaction (1C) or (2C), and it is suggested that (1C) occurs by a concerted mechanism:

$$(CH_3)_3CC(CH_3)_2 \rightarrow i-C_4H_8 + i-C_3H_7$$
(1C)

$$(CH_3)_3CC(CH_3)_2 + O_2 \rightarrow (CH_3)_3CC(CH_3) = CH_2 + HO_2.$$

$$(2C)$$

Rate constants have been obtained for a number of the homolysis reactions of the trimethylbutyl radicals, for which there is a good correlation between $\log k$ and ΔU , the internal energy change.

For the quantitative interpretation of the oxidation of alkanes, it is necessary to know the proportions of each species of alkyl radical formed in the primary radical attack on the alkane, for example, the proportions of 1-pentyl, 2-pentyl, and 3-pentyl radicals from pentane.¹ At present, the calculation of the proportions is based on two assumptions. (i) All primary C—H bonds, all secondary C—H bonds and all tertiary C—H bonds in alkanes are equivalent when attacked by radicals. (ii) The total rate constant for radical attack on alkanes is the sum of the rate constants for attack at each individual C—H bond. The rotal rate constant for attack by a radical is then given by eqn (i),

$$k_{\rm t} = n_{\rm p} A_{\rm p} \exp(-E_{\rm p}/RT) + n_{\rm s} A_{\rm s} \exp(-E_{\rm s}/RT) + n_{\rm t} A_{\rm t} \exp(-E_{\rm t}/RT)$$
(i)

where subscripts p, s and t refer to attack at primary, secondary and tertiary C—H bonds, n is the number of C—H bonds and A is the pre-exponential factor per C—H bond. Expressions of this form are available for the reactions of O,² H³ and OH³ with linear and moderately branched alkanes. However, comparison of results obtained⁴ with ethane, neopentane and tetramethylbutane suggests that the simple additivity rule breaks down with highly branched alkanes.

The product distribution when tetramethylbutane is added⁴ to slowly reacting mixtures of $H_2 + O_2$ at 480 °C is considerably different from that for linear alkanes and suggests that the radicals from highly branched alkanes undergo rapid homolysis due to steric strain. Virtually no rate data are available on the decomposition or oxidation reactions of alkyl radicals containing more than five carbon atoms, particularly the highly branched species.

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To obtain more information on the reactions of highly branched alkane systems, studies have been carried out on the addition of 2,2,3-trimethylbutane to slowly reacting mixtures of $H_2 + O_2$ in aged boric-acid-coated vessels. Unlike tetramethylbutane, formation of a conjugate alkene is possible and by measurement of its yield relative to those of other products, the rate constants of a number of elementary reactions may be determined.

EXPERIMENTAL

The apparatus and general procedure have been described elsewhere.⁵ Pressure measurements were recorded by coupling the output from a Southern Electronics SE 180 pressure transducer to a recorder; maximum sensitivity corresponded to a full-scale deflection of 1 mV for a pressure difference of 1 Torr. Apart from formaldehyde, which was determined colorimetrically,⁶ the concentrations of all products were measured gas chromatographically. No analysis was made for peroxides or H₂O. A cylindrical Pyrex vessel, 5.2 cm in diameter and 20 cm in length, coated with boric acid, and aged by repeated H₂+O₂ reactions was used at 480 °C.

RESULTS

KINETIC RESULTS

To minimise changes in the relative concentrations of H, O, OH and HO₂ radicals, 0.025% of 2,2,3-trimethylbutane (TRIMB) has been used in the kinetic studies. The relative rates of loss of TRIMB and H₂ have been measured experimentally over a wide range of mixture composition, for TRIMB by gas chromatography and for H₂ by measurement of the pressure change accompanying the overall reaction $2H_2+O_2=2H_2O$. As found for other alkanes,³ d[TRIMB]/d[H₂] is affected more by change in H₂ pressure than by change in the pressure of O₂. As previously, ³⁻⁵ the pressure change, ΔP_{50} , corresponding to 50% loss of TRIMB has been used as a measure of d[TRIMB]/d[H₂]. The values of ΔP_{50} are corrected for the positive pressure change, $\Delta P(\text{TRIMB})_{50}$, accompanying the oxidation of TRIMB. The calculation of $\Delta P(\text{TRIMB})_{50}$ is based on the product distribution, determined over a wide range of mixture composition, which is presented later. As the values of $\Delta P(\text{TRIMB})_{50}$ so determined vary between 3% and 11% of ΔP_{50} , slight uncertainty in $\Delta P(\text{TRIMB})_{50}$ should not lead to an error in excess of 2% in the final values of ΔP_{50} .

A computer program was used to calculate ΔP_{50} and to obtain the root-mean-square deviation between the observed and calculated values. A comprehensive mechanism was used for the H₂+O₂ reaction,³ and allowance was made for the slight self-heating (0.5-1.0 °C) that occurs. Allowance was also made for the removal of TRIMB by the direct unimolecular process (A),⁷ which accounts for *ca.* 1% of the TRIMB consumed at ΔP_{50}

$$(CH_3)_3CCH(CH_3)_2 \rightarrow t - C_4H_9 + i - C_3H_2.$$
(A)

TRIMB is removed mainly by H and OH attack and to a lesser extent by reaction with O and HO₂ radicals. These reactions enter the computer program³ as ratios, k_{21}/k_1 , k_{22}/k_2 , k_{23}/k_3 and $k_{24}/k_{10}^{\frac{1}{2}}$:

$$OH + TRIMB \rightarrow C_7 H_{15} + H_2 O \qquad (21)^*$$

$$H + TRIMB \rightarrow C_7 H_{15} + H_2 \tag{22}$$

$$O + TRIMB \to C_2 H_{15} + OH$$
 (23)

* The equation numbers used are consistent with previous publications.

$$HO_2 + TRIMB \rightarrow C_7H_{15} + H_2O_2$$
(24)

$$OH + H_2 \rightarrow H + H_2O \tag{1}$$

$$H + O_2 \rightarrow O + OH$$
 (2)

$$O + H_2 \to OH + H \tag{3}$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2. \tag{10}$$

As reactions (23) and (24) are of minor importance, the best available estimates of $k_{23}/k_3 = 96^{2.8}$ and $k_{24}/k_{10}^{\frac{1}{2}} = 4.5^7$ (dm³ mol⁻¹ s⁻¹)^{1/2} were considered sufficiently accurate. By use of an optimisation procedure,³ minimum r.m.s. deviation of 5.7% was obtained with optimum values of $k_{21}/k_1 = 12.2$ and $k_{22}/k_2 = 257$ for the range of mixtures given in table 1. The sensitivity of these values to changes in k_{23}/k_3 and $k_{24}/k_{10}^{\frac{1}{2}}$ is shown in table 2; the value of k_{21}/k_1 is more affected than that of k_{22}/k_2 , and error limits of ± 1.5 and ± 10 , respectively, are suggested.

TABLE 1.—PRESSURE CHANGES CORRESPONDING TO 50% CONSUMPTION OF TRIMB (ALL PRESSURES IN TOTY)

	mixture composition				
H_2	O ₂	N ₂	TRIMB	ΔP_{50} obs.	ΔP_{50} calc.
140	70	290	0.125	0.89	0.85
210	70	220	0.125	1.13	1.12
280	70	150	0.125	1.43	1.38
360	70	70	0.125	1.67	1.66
430	70	0	0.125	1.85	1.90
140	140	220	0.125	1.00	1.14
140	210	150	0.125	1.29	1.28
140	280	80	0.125	1.40	1.37
140	360	0	0.125	1.53	1.43
			r.m.s. de	viation	5.7%

Table 2.—Sensitivity of the optimum values of k_{21}/k_1 and k_{22}/k_2 to changes in k_{23}/k_3 and $k_{24}/k_{10}^{\frac{1}{2}}$

		1 (1 1)	optimur		
	k_{23}/k_{3}	$(dm^3 mol^{-1} s^{-1})^{\frac{1}{2}}$	k_{21}/k_1	k_{22}/k_{2}	r.m.s. deviation (%)
_	96 ^a	4.5ª	12.2	257	5.7
	96	5.6	10.0	242	5.7
	96	3.3	14.8	273	5.6
	72	4.5	13.5	256	5.7
	120	4.5	11.2	259	5.7

^a Recommended values.

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Absolute values of k_{21} and k_{22} may be determined as follows. Baldwin and Walker³ give $k_1 = 1.28 \times 10^5 T^{1.5} \exp(-1480/T) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ over the temperature range 300-900 K, based on fitting a slight curve to points obtained by Greiner,⁹ and Eberius *et al.*,¹⁰ and by Westenberg and de Haas.¹¹ From this expression, $k_1 = 3.71 \times 10^8$, which gives $k_{21} = 4.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 480 °C. By use of flash photolysis and kinetic spectroscopy, Greiner¹² has determined k_{21} between 300 and 500 K, although the results are scattered, and combination with the present value gives the reasonable overall Arrhenius parameters $A_{21} = (5.92 \pm 0.50) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $E_{21} = 1800 \pm 350 \text{ J mol}^{-1}$.

Combination of $k_{22}/k_2 = 257$ with $k_{22e}/k_2 = 44$, from addition studies with ethane,³ and with $k_{22e} = 1.32 \times 10^{11} \exp(-4715/T)$ obtained by Camilleri, Marshall, and Purnell¹³ gives $k_{22} = 1.48 \times 10^9$ dm³ mol⁻¹ s⁻¹ at 480 °C. No other value for k_{22} is available, but $k_{22ib} = 1.28 \times 19^9$ for overall H atom attack on isobutane,³ which also contains a tertiary C—H bond:

$$H + C_2 H_6 = H_2 + C_2 H_5$$
 (22e)

$$H + i - C_4 H_{10} = H_2 + C_4 H_9.$$
 (22ib)

With linear alkanes, reasonably accurate values for the total rate constant for radical attack may be obtained^{2, 3, 12} from eqn (i). However, recent work⁴ shows that simple extrapolation to highly branched alkanes is not possible. Thus for OH attack at 480 °C, k_{21}/k_1 is 6.0, 10.2 and 8.0 for ethane, neopentane and tetramethylbutane, respectively, and for H attack k_{22}/k_2 is 44, 52 and 112, respectively, compared with relative values of 1:2:3 predicted for the alkanes by simple additivity.

It is not possible to partition total reaction with TRIMB unequivocally into attack at primary C—H and tertiary C—H bonds, but because of the similarity in structure it may be assumed that all CH₃ groups in TRIMB and tetramethylbutane are equivalent. Consequently, the rate constant for attack at the tertiary C—H bond in TRIMB is obtained by subtracting five-sixths of that for tetramethylbutane from the total rate constant for TRIMB. On this basis, the specific ratios $k_{21}^t/k_1 = 5.5$ and $k_{21}^p/k_1 = 6.7$ are obtained for OH attack on TRIMB and $k_{22}^t/k_2 = 164$, $k_{22}^p/k_2 = 93$ for H atom attack at 480 °C. Isobutane is the only other alkane for which comparable values are available³ at 480 °C. Taking three-quarters of the appropriate rate constant ratios for neopentane³ as the primary C—H bond contribution in isobutane, then $k_{21}^t/k_1 = 5.0$ and $k_{22}^t/k_2 = 184$, in excellent agreement with the values for tertiary attack in TRIMB.

If the same treatment is applied at the lower temperatures used by Greiner,¹² fig. 1 shows that the values obtained for k_{21}^t from isobutane and TRIMB differ by a factor of 2, although the values converge with opposing slopes as the temperature is raised towards 480 °C. Based on the lines drawn in fig. 1, then for TRIMB, $\log_{10} (A_{21}^t/dm^3 \text{ mol}^{-1} \text{ s}^{-1}) = 9.23 \pm 0.09, E_{21}^t = -960 \pm 800 \text{ J mol}^{-1}$, and for isobutane, $\log_{10} (A_{21}^t/dm^3 \text{ mol}^{-1} \text{ s}^{-1}) = 9.41 \pm 0.09, E_{21}^t = 2250 \pm 800 \text{ J mol}^{-1}$. The points at *ca*. 370 K for TRIMB are ignored here because the Arrhenius plot for the **total** rate constant for reaction (21) should show an increasing gradient due to the increasing contribution from attack at the primary C—H bonds as the temperature is raised, and this would not occur if the 370 K point is included.

The reason for the difference in the two sets of parameters for k_{21}^t is not clear. Use of results for ethane or neopentane to calculate the contribution from primary attack would not seriously affect the discrepancy at room temperature. As pointed out, the discrepancy decreases at higher temperatures, and a value of $k_{21}^t = 1.6 \times 10^9$ dm³ mol⁻¹ s⁻¹ between 270 and 1500 K would not be in error by > 60%. From a

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FIG. 1.—Arrhenius plot for OH attack on a tertiary C—H bond. Isobutane results: ●, present work; ○, Greiner¹². TRIMB results: ▲, present work; △, Greiner¹².

		Ι		II	III	
mixture compound	concentration (absolute percentage)					
TRIMB	0.9000	0.7000	0.5000	0.9000	0.9000	
i-butene	0.0784	0.1480	0.1710	0.0553	0.0750	
propene	0.0697	0.1510	0.2220	0.0527	0.0675	
i-butene oxide	0.0012	0.0047	0.0109	0.0006	0.0011	
propene oxide	0.0031	0.0079	0.0121	0.0030	0.0029	
2,3,3-trimethylbut-1-ene	0.0129	0.0257	0.0295	0.0320	0.0133	
2,3-dimethylbut-1-ene	0.0018	0.0051	0.0073	0.0015	0.0018	
2,3-dimethylbut-2-ene	0.0012	0.0037	0.0068	0.0022	0.0012	
3,3-dimethylbut-1-ene	0.0006	0.0014	0.0019	0.0007	0.0006	
2,2,3,3-tetramethyloxetan	0.0019	0.0049	0.0057	0.0033	0.0020	
3,3,4-trimethyltetrahydrofuran	0.0004(0)	0.0012	0.0021		0.0004	
3-methylbutan-2-one	0.0003	0.0010	0.0025	0.0002	0.0003	
formaldehyde	0.0193	0.0305	0.0385	0.0217	0.0138	
carbon monoxide	0.0053	0.0505	0.2020	0.0100	0.0050	
carbon dioxide	0.0009	0.0055	0.0160	0.0024	0.0010	
acetone	0.0012	0.0095	0.0610	0.0006	0.0013	
ethylene	0.0001	0.0110		0.0000	0.0001	
methane	0.0070	0.0750	0.2100	0.0034	0.0077	

TABLE 3.—PRODUCT YIELDS FOR MIXTURES I, II AND III



fraction TRIMB consumed

FIG. 2.—Variation of products with loss of TRIMB. $H_2 = 140$, $O_2 = 70$, $N_2 = 285$, TRIMB = 5 Torr; 480 °C. (a) \bigcirc , TMO; \times , isobutene oxide; \textcircledline , TMTHF. (b) \bigcirc , CH₃COCH₃; \times , CO₂; \textcircledline , 23DMB-1. (c) \bigcirc , TRIMB-1; \Box , HCHO; \times , DMB-2; \textcircledline , 33DMB-1; \bigtriangleup , propene oxide. (d) \bigcirc , isobutene; \times , propene; \textcircledline , CH₄; \bigtriangleup , CO.

mean gradient (dotted line) then $\log_{10}(A_{21}^t/dm^3 \text{ mol}^{-1} \text{ s}^{-1}) = 9.32 \pm 0.13$ and $E_{21}^t = 460 \pm 950 \text{ J mol}^{-1}$, and these parameters are recommended for general use with alkanes in the temperature range 300-1 500 K.

ANALYTICAL RESULTS

A complete analysis was carried out for the three basic mixtures containing 5 Torr of TRIMB, the standard mixture (I), $O_2 = 70$, $H_2 = 140$, $N_2 = 285$, one of high O_2 content (II), $O_2 = 355$, $H_2 = 140$, and one of high H_2 content (III), $O_2 = 70$,

absolute percentage

 $H_2 = 425$ Torr. Table 3 shows the absolute percentages of the products as a function of TRIMB consumed for mixture I, and the absolute percentages at 10% consumption for mixtures II and III. In general, with the possible exception of HCHO, the product distributions for mixtures I and III are almost identical, but change in O_2 pressure has a greater effect. Primary products can usually be distinguished easily from the shapes of their profiles, which are shown in fig. 2 for mixture I. All the products listed in table 3, except CO, CO₂ and ethylene, appear to be formed in primary processes, although a number are also formed as secondary products. In this paper only the primary products, formed in the initial stages of reaction, will be discussed.

Isobutene and propene, formed in nearly equal amounts, are the major initial products, although their yield drops noticeably at high O_2 pressures, where 2,3,3-trimethylbut-1-ene is formed in *ca.* 30% yield. In contrast to tetramethylbutane as additive,⁴ where no conjugate O-heterocyclic compounds were detected, 2% of the TRIMB initially consumed was converted to 2,2,3,3-tetramethyloxetan. Traces of 3,3,4-trimethyltetrahydrofuran were also found.

DISCUSSION OF ANALYTICAL RESULTS

Radical attack on TRIMB produces three species of alkyl radical:

$(CH_3)_2C-CH(CH_3)_2$	$(CH_3)_3C$ — $CH(CH_3)CH_2$	$(CH_3)_3C - C(CH_3)_2$
CH ₂		
(A)	(D)	(\mathbf{C})
(A)	(D)	(C)

For a quantitative interpretation of the initial product distribution, the proportions of each of the three species of alkyl radical formed must be known for all mixtures used. From the rate constant ratios specified earlier for reactions (21)-(24) and on the assumption, discussed in the kinetics section, that all the CH₃ groups in TRIMB and tetramethylbutane are equivalent, the computer program gives the proportions of radicals A, B and C formed during the first 5% consumption of TRIMB indicated in table 4 for mixtures I, II and III. The proportion of radicals produced is not particularly sensitive to mixture composition.

		propo	ortions	
mixture	A (%)	B (%)	C (%)	homolysis ^a
I	18.1	12.1	69.2	0.6
II	17.2	11.5	70.6	0.7
III	16.6	11.0	72.0	0.4

TABLE 4.—PROPORTIONS OF RADICALS A, B AND C FORMED DURING INITIAL 5% REACTION

^{*a*} Due to the reaction $(CH_3)_3CCH(CH_3)_2 \rightarrow t-C_4H_9+i-C_3H_7$.

The final conclusions as to the products formed from each radical, together with the approximate initial yields for the standard mixture, are summarized in Appendix I, to which reference is made in the rest of the paper.

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FORMATION OF ISOBUTENE AND 2,3,3-TRIMETHYLBUT-1-ENE

Since isobutene and propene are the major initial products for all three mixtures, decomposition of the trimethylbutyl radicals must be the dominating process. In radicals A and B, homolysis of the central bond will occur very readily because of steric strain which results in endothermicities of only *ca*. 68 and 62 kJ mol⁻¹ for reactions (1 A) and (1 B), compared with values of *ca*. 100 kJ mol⁻¹ for the decomposition of $n-C_3H_7$, $n-C_4H_9$, $s-C_4H_9$ and $i-C_4H_9$ radicals:

$$A \rightarrow i - C_4 H_8 + i - C_3 H_7 \tag{1A}$$

$$B \rightarrow C_3 H_6 + t - C_4 H_9. \tag{1B}$$

Under the present conditions, 99% of both t- $C_4H_9^{14}$ and i- $C_3H_7^{15}$ radicals react with O_2 to give conjugate alkene, the rest giving isobutene oxide and propene oxide, respectively. Formation of the alkenes *via* homolysis of radical C must involve an H atom transfer, which may well occur in a concerted step involving a 1,4 cyclic transition state similar to that

$$(CH_3)_3CC(CH_3)_2 \rightarrow (CH_3)_2 C--C(CH_3)_2 \rightarrow i-C_4H_8+i-C_3H_7 \qquad (1C)$$

$$H_3C--H$$

suggested for the molecular decomposition of tetramethylbutane into isobutane and isobutene.¹⁶

Reaction (2C) is almost certainly the major source (Appendix I) of 2,3,3-trimethylbut-1-ene (TRIMB-1) which is formed in *ca.* 12% yield in mixtures I and III and 30% yield in the high O_2 mixture II. The relative rate of formation of TRIMB-1 and isobutene from radical C is then given by eqn (ii):

$$d[TRIMB-1]_{c}/d[isobutene]_{c} = k_{2C}[O_{2}]/k_{1C}$$
(ii)

$$(CH_3)_3CC(CH_3)_2 + O_2 \rightarrow (CH_3)_3CC(CH_3) = CH_2 + HO_2.$$
(2C)

Assuming that radicals A and B solely undergo reactions (1 A) and (1 B), respectively, then the partial pressure of isobutene arising from radical C is given by eqn (iii),

$$[\text{isobutene}]_{c} = [\text{isobutene}]_{obs} - [A]_{f} - [B]_{f}$$
(iii)

where $[A]_f$ and $[B]_f$ are the pressures of TRIMB consumed which give rise to radicals A and B, respectively. Use of the figures in table 4 then permits the calculation of [isobutene]_e. At 5% consumption, [TRIMB-1]_e/[isobutene]_e = 0.27 at $O_2 = 70$ Torr (mixtures I and III) and 1.2 at $O_2 = 355$ Torr (mixture II). Unfortunately, with the high O₂ mixture the calculation of [isobutene]_e involves the difference of two similar quantities and is accurate to only ca. 25%. Nevertheless, the variation in the ratio is sufficiently marked to provide support for the proposed mechanism. Later it is shown that a small fraction of radicals A and B form compounds other than isobutene (Appendix I). When allowance is made for this, the value of the ratio changes from 0.27 to 0.26 at $O_2 = 70$ and from 1.2 to 1.1 at $O_2 = 355$ Torr. Use of the more accurate value at low O₂ gives $k_{2C}/k_{1C} = 175 \pm 20$ dm³ mol⁻¹. No independent values of the ratio or of the absolute rate constants are available. Recent work¹⁷ has established that the rate constants for the reaction of alkyl radicals with O₂ to give conjugate alkene show a consistent pattern, and by consideration of the values for C_2H_5 , i- C_3H_7 , s-C₄H₉ and t-C₄H₉, where only primary C-H bonds are involved in the abstraction, a value of $k_{2C} = (1.3 \pm 0.2) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ is suggested. Combination with $k_{2C}/k_{1C} = 175 \text{ dm}^3 \text{ mol}^{-1}$ then gives $k_{1C} = (7.4 \pm 2.5) \times 10^5 \text{ s}^{-1}$.

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As already noted, reaction (1C) is similar to the molecular decomposition of tetramethylbutane into isobutane and isobutene.¹⁶ Although no such reaction has been reported previously for radicals, this is not surprising since the products from such a decomposition for simple radicals can be formed more easily by simple C—C bond fission, and little information exists on the decomposition of large branched radicals. The only alternative is to assume that radical C is not formed at all and to account for the O₂ dependence of the [TRIMB-1]/[i-C₄H₈] in terms of reaction with O₂ and decomposition of radical B. However formation of even 10% of radical C would destroy this O₂ dependence, and it seems unlikely that the yield of C is anywhere near as low as this.

Reaction (1 C) is unlikely to proceed through the initial formation of radical A via a 1,3 H atom shift for two reasons. (i) Based¹⁸ on values for 1,4 H shift in 1-pentyl and for 1,5 H shift in 1-hexyl radicals, then even for irreversible formation of A and C the value of k_{1C} will then not exceed 1×10^2 s⁻¹, compared with the experimental value of 7.4 × 10⁵. (ii) Since ΔS^{\neq} for the 1,3 shift is close to zero, absolute rate theory gives the A factor as ca. $ekT/h = 10^{13.6}$ s⁻¹ at 480 °C. Combination of this value with the observed value for k_{1C} gives an activation energy for the 1,3 H shift involved of 110 kJ mol⁻¹, at least 50 kJ mol⁻¹ lower than expected since the strain energy alone in the ring transition state is ca. 100 kJ mol⁻¹. For the concerted step suggested, $A \simeq ekT/h$ and an activation energy of ca. 110 kJ mol⁻¹ is not unreasonable.

FORMATION OF 2,3-DIMETHYLBUT-2-ENE

Studies⁷ of the decomposition of TRIMB in the presence of O_2 in KCl-coated vessels at 500 °C, where attack of HO₂ radicals at the weak tertiary C—H bond markedly favours formation of radical C, suggest that 2,3-dimethylbut-2-ene (DMB-2) is formed by methyl loss from radical C reaction (3C). If there is no other source, then the relative rate of formation of DMB-2 and TRIMB-1 is given by eqn (iv):

$$d[TRIMB-1]/d[DMB-2] = k_{2C}[O_2]/k_{3C}$$
 (iv)

$$(CH_3)_3CC(CH_3)_2 \rightarrow (CH_3)_2C = C(CH_3)_2 + CH_3.$$
(3C)

However, in the present work the initial value of the product ratio only increases from 10.8 at $O_2 = 70$ to 15.7 at $O_2 = 355$ Torr. Also, from⁷ $k_{3C} = 1.4 \times 10^3$ s⁻¹ at 500 °C with $E_{3C} = 158$ kJ mol⁻¹ (see table 5) and $k_{2C} = 1.3 \times 10^8$ dm³ mol⁻¹ s⁻¹ at 480 °C, given earlier, the calculated initial ratio of [TRIMB-1]/[DMB-2] at 480 °C is 270 at $O_2 = 70$ Torr and 1370 at $O_2 = 355$ Torr. Little DMB-2 is therefore formed from radical C by reaction (3C), and the sequence (p. 2166) involving radical A is suggested as the only other simple route.

The proposed mechanism is difficult to confirm, but the following points may be noted in support. (i) The initial value of the product ratio [TMO]/[DMB-2], where TMO is 2,2,3,3-tetramethyloxetan, only changes from 1.9 at $O_2 = 70$ Torr to 1.7 at $O_2 = 355$ Torr consistent with the zero oxygen dependence predicted. (ii) The acetone profile, and the fact that acetone is a primary product from isobutene,¹⁹ suggests that it is formed mainly, if not exclusively, as a secondary product. In confirmation, the ratio [acetone]/([TMO]+[DMB-2]) at 5% consumption decreases from 0.08 to 0.03 as O_2 increases from 70 to 355 Torr, in contrast to the five-fold increase predicted. It is concluded that acetone formation by reaction (8A) is negligible. This is consistent with studies using tetramethylbutane as additive,⁴ which show that addition of O_2 to the highly strained QOOH radical cannot compete with decomposition.



The pressure of DMB-2 formed from radical A is given by eqn (v),

$$[DMB-2] = [A_f] k'_{5A} [O_2] \{ k_{7A} / (k_{6A} + k_{7A}) \} / (k_{1A} + k'_{5A} [O_2] + k_{3A})$$
(v)

where $[A]_{f}$ is the pressure of TRIMB consumed which gives the A radical. k'_{5A} is the overall rate constant for the formation of the alkylhydroperoxide radical $(CH_3)_2C(CH_2OOH)C(CH_3)_2$, defined by the equation

$$d[(CH_3)_2C(CH_2OOH)C(CH_3)_2]/dt = k'_{5A}[(CH_3)_2C(CH_2)CH(CH_3)_2][O_2].$$

If reaction (4A) is assumed to be effectively equilibrated, $k'_{5A} = K_{4A}k_{5A}$. Since $(k'_{5A}[O_2]+k_{3A})$ is significantly smaller than k_{1A} (see Appendix I), eqn (v) simplifies

$$[DMB-2] = [A]_{f} k_{5A} K_{4A} [O_{2}] \{ k_{7A} / (k_{6A} + k_{7A}) \} / k_{1A}.$$
(vi)

Since radical B is only formed in ca. 11% yield, and will predominantly decompose to $(CH_3)_3C$ and C_3H_6 , the high yield (ca. 12%) of TRIMB-1 must arise predominantly from the C radical. The pressure of TRIMB-1 formed in this way is given by eqn (vii),

$$[TRIMB-1] = [C]_{f} k_{2C}[O_{2}]/(k_{1C} + k_{2C}[O_{2}]) \simeq [C]_{f} k_{2C}[O_{2}]/k_{1C}$$
(vii)

since k_{1C} is greater than $k_{2C}[O_2]$. As [A]_f and [C]_f are effectively independent of O_2 concentration (table 4), the [O₂] terms in the ratio [DMB-2]/[TRIMB-1] from eqn (vi) and (vii) cancel, consistent with the observation that the ratio changes little for a five-fold variation in O_2 concentration. (iii) Based on the mechanism, the relative rates of formation of isobutene, TMO, and DMB-2 from radical A are related by eqn (viii)

$$\{d[i-butene]/d([TMO]+[DMB-2])\}_{A} = k_{1A}/K_{4A}k_{5A}[O_{2}].$$
 (viii)

If there are no other reaction pathways for radical A, then in the early stages of

reaction where product consumption may be ignored, the partial pressure of i-butene formed from radical A is given by eqn (ix)

$$[i-butene]_{A} = [A]_{f} - X[TMO] - Y[DMB-2] - Z[23DMB-1]$$
 (ix)

where X, Y and Z are the fractions of TMO, DMB-2 and 2,3-dimethylbut-1-ene (23DMB-1) formed from radical A, respectively. Formation of DMB-2 from radical B is not plausible and, as shown above, formation from radical C is negligible, so that Y = 1. Formation of TMO from radical C is possible, but would involve a rather slow¹⁸ 1,5 H-atom transfer in the $(CH_3)_3CC(CH_3)_2O_2$ radical which could not compete efficiently with loss of O_2 , so that X = 1. No other route for the formation of DMB-1 is plausible, so that Z = 1. By use of the proportions of radical A formed (table 4), together with the yields of products at 5% consumption, then {d[i-butene]/ $d([TMO] + [DMB-2]))_A$ is 8.2 at $O_2 = 70$ Torr and 2.6 at $O_2 = 355$ Torr. The change in the ratio with O₂ is rather lower than predicted by eqn (viii), and it is difficult to find an acceptable reason. The combined yields of TMO, DMB-2, and 23DMB-1 do not exceed ca. 25% of $[A]_f$, so that $[i-butene]_A$ should be obtained reasonably accurately from eqn (ix) unless radical A gives another product of some importance or [A]_f is seriously in error. As discussed earlier, some error in the calculated proportions of radicals A, B and C is possible, but the reduction of $[A]_f$ by a factor of over three would be necessary for agreement with the predicted variation. Such a reduction would only be possible in the unlikely event that the rates of attack by H and OH at the CH_a groups at the two ends of TRIMB are markedly different. If the mechanism is accepted, the results for mixture I, which are confirmed by those of mixture III, and which are less sensitive to the value of $[A]_r$, may be used to give a reasonably reliable rate constant for reaction (1A).

Use of Benson's²⁰ additivity data gives a calculated value of $K_{4A} = 90 \text{ dm}^3 \text{ mol}^{-1}$ at 480 °C and Benson²¹ has suggested that $k_{4A} \approx 1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, so that $k_{-4A} \approx 1.1 \times 10^7 \text{ s}^{-1}$. A value of $2.2 \times 10^6 \text{ s}^{-1}$ has been suggested¹⁸ for a 1,5t H-atom transfer such as that in reaction (5A) so that, within the limits of accuracy appropriate here, reaction (4A) may be regarded as effectively equilibrated. With $\{d[i\text{-butene}]/d([\text{TMO}]+[\text{DMB-2}])\}_A = 8.3$ at $O_2 = 70 \text{ Torr}$, eqn (viii) gives $k_{1A} = 2.4 \times 10^6 \text{ s}^{-1}$, with a probable accuracy of *ca.* 25%.

FORMATION OF 2,3-DIMETHYLBUT-1-ENE (23DMB-1)

Loss of a methyl group from radical A by reaction (3A) is the only simple route for the formation of 23DMB-1. The relative rate of formation of i-butene and 23DMB-1 from radical A is then given by eqn (x):

$$(d[i-butene]/d[23DMB-1])_{A} = k_{1A}/k_{3A}.$$
 (x)

Initial values of the product ratio of 9.6, 9.1 and 11.5 are obtained for mixtures I, II and III, respectively. As predicted by eqn (x), the values are independent of mixture composition, the mean value being 10.1. The order of magnitude difference in the rate constants for the two homolyses is consistent with the considerably greater strain in the central C—C bond. From $k_{1A} = 2.4 \times 10^6 \text{ s}^{-1}$ above, $k_{3A} = 2.4 \times 10^5 \text{ s}^{-1}$.

FORMATION OF 3,3-DIMETHYLBUT-1-ENE AND 3,3,4-TRIMETHYLTETRAHYDROFURAN

3,3-dimethylbut-1-ene (33DMB-1) and 3,3,4-trimethyltetrahydrofuran (TMTHF) are formed from radical B as shown in the following scheme, which is based on previously established^{4, 18} reactions.



Assuming that the three types of H-atom transfers in the $(CH_3)_3CCH(CH_3)CH_2O_2$ radical occur at the same relative rate as in the lower, linear alkanes,¹⁸ then the relative rates of reactions (6B), (7B) and (5B) are 1:3.3:15. Thus if TMTHF is the only significant product formed through reaction (7B), as is likely, then only negligible quantities of 33DMB-1 are formed *via* reaction (10B) even if all radicals undergoing reaction (6B) give the alkene. From the estimated yield (Appendix 1) of 0.2% of TMTHF from reaction (7B), *ca.* 1% of 2-methyl-2-t-butyloxiran would be expected *via* reaction (5B) since $k_{5B}/k_{7B} \simeq 4.5$. The absence of 2-methyl-2-t-butyloxiran experimentally is attributed to the strain of ring formation, accentuated by the t-butyl side group, which makes its formation unlikely. A similar absence of O-ring compounds is apparent in the oxidation of tetramethylbutane.⁴ Alternative reactions of the particular QOOH radical involved are difficult to specify, but may include H-atom transfer back to the peroxy radical (-5B) or loss of HO₂ to give TRIMB-1. If the latter is dominant, the TRIMB-1 formed in this way will be small (< 1%) compared with the overall yield (*ca.* 12%) of the alkene, so that previous calculations will be materially unaffected.

TMTHF is formed from QOOH radicals arising from both radical A and radical B. Both routes involve 1,6p H-atom transfers preceded by reversible steps which on the basis of calculations using Benson's²⁰ additivity rules have effectively the same value of the equilibrium constant. Radicals A and B are removed mainly through homolysis of the strained central C—C bonds with very similar rate constants. It is therefore proposed that TMTHF is formed equally from radicals A and B, the greater proportion of A formed initially being balanced by the greater availability of H atoms for the 1,6p transfer in the peroxy radical formed from B.

The relative rates of formation of i-butene, 33DMB-1, and TMTHF from radical B are given by eqn (xi) and (xii):

$$(d[i-butene]/d[33-DMB-1])_{B} = k_{1B}/k_{3B}$$
 (xi)

$$(d[i-butene]/d[TMTHF])_{B} = k_{1B}/K_{4B}k_{7B}[O_{2}].$$
 (xii)

From the product yields at 5% ([i-butene]/[33DMB-1])_B = 23 at O₂ = 70 Torr, 19 at O₂ = 355 Torr, and ([i-butene]/[TMTHF])_B = 90 at O₂ = 70 Torr; gas-chromato-graphic limitations prevented the determination of this latter ratio at the higher O₂ pressure. By combining $k_{7B} = 6.0 \times 10^4 \text{ s}^{-1}$, suggested¹⁸ for the 1,6p transfer in n-C₄H₉O₂ radicals, with $K_{4B} = 220 \text{ dm}^3 \text{ mol}^{-1}$, then $k_{1B} = 1.3 \times 10^6 \text{ s}^{-1}$ at 480 °C. Use of expression (xi) then gives $k_{3B} = 6.2 \times 10^4 \text{ s}^{-1}$, with an uncertainty of at least 50%.

DISCUSSION OF RATE CONSTANTS FOR C-C HOMOLYSIS

The rate constants obtained for the various decompositions of the three species of trimethylbutyl radical are summarised in table 5(a) and (b), together with values reported previously for other radicals. Clearly, only in the cases of C_3H_7 and C_4H_9 radicals are the rate data reasonably adequate, despite the important part C—C homolyses play in the mechanisms of combustion and pyrolysis. The lack of data undoubtedly arises from the difficulty of finding suitable radical sources for quantitative studies, and frequently it has been necessary to use complex systems as in the present work.

For the trimethylbutyl radicals, fig. 3 shows that there is a reasonable correlation between ΔU and $\log_{10} k$. By application of the simple Arrhenius law $k = A \exp(-E/RT)$ and the Evans-Polanyi relation $E = a + b\Delta U$, $\log_{10} k$ and ΔU are



FIG. 3.—Plot of $\log_{10} k$ against ΔU for the decomposition of alkyl radicals. \bigcirc , trimethylbutyl; \times , tetramethylbutyl; \otimes , neopentyl; \square , propyl; \triangle , pentyl; \bigoplus , butyl.

	TABLE 5.—	-(a) DECOMPOS	SITION OF ALKY	L RADICALS AT	c 480 °C		
	reaction	Δ <i>U</i> /kJ m	ol ⁻¹ k/s ⁻¹	ref.	$E_{ m f}/{ m kJ}$ mol $(A=10^{13.8\pm0.3})$	$E_{r}/kJ \text{ mol}^{-1}$ (reverse reaction) $S_{s^{-1}}$ ($E_{r} - \Delta U$)	$E_r/kJ \text{ mol}^{-1}$ (exptl.)
(CH ₃) ₃ CC(CH ₃) ₂ (CH ₃) ₃ CCH(CH ₃)CH ₂	$\rightarrow (CH_3)_3 C = C(CH_3)_2 + CH_3 \rightarrow (CH_3)_3 + CH_3 \rightarrow (CH_3)_3 C CH = CH_2 + CH_3$	115±4 84±4	7.2×10 6.2 × 10	a 7 t present	158 ± 7 130 ± 7	43±11 46±11	32.5 ²⁸
(CH ₃), CCH(CH ₃)CH ₂	→ t-C ₄ H ₆ + C ₃ H ₆	51±4	1.3×10	bresent	7 ± 111	60 ± 11	
(CH ₃) ₂ C(CH ₂)CH(CH ₃)	² → Cn ₂ —C(Cu ₃)Cm(Cn ₃) ² + ² → i-C ₃ H, + (CH ₃) ₂ C=CH ₂	- Cn ₃ // ±4 59±4	2.4 × 10	bresent	121 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	44 ± 11 48 ± 11	
(CH ₃) ₃ CC(CH ₃) ₂ ^a	$\rightarrow i-C_3H_7 + (CH_3)_2C = CH_2$	92±4	7.4×10	5 present	114 ± 7		
(CH ₃) ₃ CC(CH ₃) ₂ CH ₂	\rightarrow t-C ₄ H ₉ +(CH ₃) ₂ CC=CH ₂	36 ± 4	1.9×10	4	108 ± 7	72 ± 11	-
(CH ₃),CC(CH ₃),CH ₂ CH CH CHCH CH	→ (CH ₃),CC(CH ₃)=CH ₂ +C	CH ₃ 70±4 100+4	1.1×10 1.6×10	4 %	140+7	70 ± 11	30.029
CH,CHCH,CH,CH,CH,	→ C,H,+C,H,	92+4	2.3×10^{-10}	38	122 + 7	30 + 11	.
(CH ₃) ₃ CCH ₂	→ (CH ₃) ₂ C=CH ₂ +CH ₃	93 ± 4	3.5×10	30	148 ± 7	55±11	30.0 ^{29'}
	^a A concerted mechanism it TABLE 5.— (b) ARRHENIUS	nvolving an H	-atom transfer FOR THE DECOM	is suggested f	or this reaction (se ower alkyl radi	e text). CALS	
	A1//k1 mol-1 4./s	-1	/k I mol ⁻¹		$E_{ m r}/{ m kJ}~{ m mol}^{-1}$	$E_{\rm r}/{\rm kJ}~{ m mol}^{-1}$	
reaction	(600 K) (exp	tl) ²⁻¹	(exptl)	ref.	$(E_{\rm f} - \Delta U)$	(iteration (exptl)	ref.
$n-C_3H_7 \rightarrow CH_3+C_2H_4$	99±4 1.6×	1014	136±2	26	37±6	32.5	29
$n\text{-}C_4H_9 \to C_2H_5 + C_2H_4$	90 ± 4 2.5 ×	1013	120±4	26	30 ± 8	30.5	29
$s-C_4H_9 \rightarrow CH_3+C_3H_6$	99±4 2.3×	1014	137±5	26	38±9	31	29
$i-C_4H_6 \rightarrow CH_3+C_3H_6$	91±4 6.3×	1013a	128 ± 7^{a}	19	37 ± 11	ł	1

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^a Based on data obtained by Trotman-Dickenson and Metcalfe,²⁷ modified as in ref. (19).

related by eqn (xiii). From fig. 3, a value of 0.90 is obtained for the constant b, which is close to the maximum value of unity expected²² for strongly endothermic processes:

$$\log_{10} k = \log_{10} A - a/2.303 RT - b\Delta U/2.303 RT.$$
(xiii)

Measurements at temperatures significantly different from 480 °C were not possible, but activation energies may be calculated from estimates of the A factors for the homolyses. From transition-state theory, the A factor for a unimolecular process is given by the standard expression (xiv), so that A is effectively determined by the value of ΔS^{\neq}

$$A = (e\mathbf{k}T/\mathbf{h})\exp\Delta S^{\neq}/\mathbf{R}.$$
 (xiv)

Rabinovitch and Setser²⁴ have specified detailed models for several transition states, and Benson and O'Neal²⁵ have used empirical methods for the calculation of ΔS^{\neq} . In both cases, values of ΔS^{\neq} marginally above zero are predicted for the homolysis of alkyl radicals. This appears to be caused mainly by a loss of entropy (*ca*. 20 J K⁻¹ mol⁻¹) due to the stiffening of one free internal rotation in the transition state which is slightly more than balanced by gains due to the lowering of several vibrational frequencies. Accepting for the decomposition of trimethylbutyl radicals the value of $\Delta S^{\neq} \approx 4 \text{ J K}^{-1} \text{ mol}^{-1}$, suggested by Benson and O'Neal²⁵ for loss of CH₃ radicals from n-C₃H₇ and s-C₄H₉ radicals, then with $ekT/h = 10^{13.6} \text{ s}^{-1}$ at 480 °C the *A* factors for the homolyses shown in table 5 become $10^{13.8 \pm 0.5} \text{ s}^{-1}$. Combination of this value with the rate constant of each homolysis at 480 °C gives the activation energies shown in table 5, the accuracy specified being due to the uncertainty of 0.5 in the value of $\log_{10} A$.

Table 5 also shows the activation energies of the reverse reactions for the addition of an alkyl group to a double bond, calculated from the values of ΔU and the activation energy of the forward process. The values are subject to considerable potential error due to the method of calculation, but are reasonably consistent with those for the lower alkyl systems, particularly as the latter are in general more exothermic.

When the rate constants for the homolysis of alkyl radicals other than the trimethylbutyl species are plotted in fig. 3, they do not fit the line drawn for the latter. A good line may be drawn through the points for the tetramethylbutyl and neopentyl homolyses with a gradient which corresponds to $b \simeq 1$. Rate constants for the pentyl radicals and for the propyl and butyl radicals appear to fall on separate lines, but the spread in the rate constants is too small to establish a value of b.

- ¹ R. R. Baldwin, J. P. Bennett and R. W. Walker, 16th Int. Combustion Symp. (The Combustion Institute, Pittsburgh, 1977), p. 1041.
- ² J. T. Herron and R. E. Huie, J. Phys. Chem. Ref. Data, 1973, 2, 467.
- ³ R. R. Baldwin and R. W. Walker, J. Chem. Soc., Faraday Trans. 1, 1979, 75, 140.
- ⁴ R. R. Baldwin, R. W. Walker and R. W. Walker, J. Chem. Soc., Faraday Trans. 1, 1979, 75, 1447.
- ⁵ R. R. Baldwin, D. E. Hopkins and R. W. Walker, Trans. Faraday Soc., 1970, 66, 189.
- ⁶ C. E. Bricker and H. R. Johnson, Ind. and Eng. Chem. (Anal.), 1945, 19, 400.
- ⁷ R. R. Baldwin, R. W. Walker, and R. W. Walker, J. Chem. Soc., Faraday Trans. 1, 1980, 76, 825.
- ⁸ D. L. Baulch, D. D. Drysdale, D. G. Horne and A. C. Lloyd, *Evaluated Kinetic Data for High Temperature Reactions* (Butterworth, London, 1972), vol. 1.
- ⁹ N. R. Greiner, J. Chem. Phys., 1969, 51, 5049.
- ¹⁰ K. H. Eberius, K. Hoyermann and H. Gg. Wagner, 13th Int. Combustion Symp. (The Combustion Institute, Pittsburgh, 1971), p. 713.
- ¹¹ A. A. Westenberg and N. de Haas, J. Chem. Phys., 1973, 58, 4061.
- ¹² N. R. Greiner, J. Chem. Phys., 1970, 53, 1070.
- ¹³ P. Camilleri, R. M. Marshall and J. H. Purnell, J. Chem. Soc., Faraday Trans. 1, 1974, 70, 1434.

Published on 01 January 1981. Downloaded by Northeastern University on 22/10/2014 22:53:16.

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- ¹⁴ G. Atri, R. R. Baldwin, G. A. Evans and R. W. Walker, J. Chem. Soc., Faraday Trans. 1, 1978, 74, 366.
- ¹⁵ R. R. Baldwin, C. J. Cleugh, J. C. Plaistowe and R. W. Walker, J. Chem. Soc., Faraday Trans. 1, 1979, **75**, 1433.
- ¹⁶ R. R. Baldwin, G. A. Evans and R. W. Walker, J. Chem. Soc., Faraday Trans. 1, 1978, 74, 1329.
- ¹⁷ G. A. Evans and R. W. Walker, J. Chem. Soc., Faraday Trans. 1, 1979, 75, 1458.
- ¹⁸ R. W. Walker, *Reaction Kinetics* (Spec. Period. Rep., The Chemical Society, London, 1975), vol. 1, p. 161.
- ¹⁹ R. R. Baker, R. R. Baldwin and R. W. Walker, J. Chem. Soc., Faraday Trans. 1, 1978, 74, 2229.
- ²⁰ S. W. Benson and R. Shaw, Organic Peroxides, ed. D. Swern (Wiley, New York, 1970), vol. 1, p. 105.
 ²¹ S. W. Benson, The Mechanisms of Pyrolysis, Oxidation and Burning of Organic Compounds, N.B.S. Spec. Publ. 357 (U.S. Dept. of Commerce, Washington, D.C., 1972), p. 121.
- ²² R. R. Baldwin and R. W. Walker, J. Chem. Soc., Perkin Trans. 2, 1973, 361.
- 23 R. R. Baldwin, J. P. Bennett and R. W. Walker, J. Chem. Soc., Faraday Trans. 1, 1980, 76, 1075.
- ²⁴ B. S. Rabinovitch and D. W. Setser, Advances in Photochemistry (Wiley Interscience, New York, 1964), vol. 3, p. 1.
- ²⁵ S. W. Benson and H. E. O'Neal, *Kinetic Data on Gas Phase Unimolecular Reactions*, NSRDS-NBS21 (U.S. Government Printing Office, Washington, D.C., 1970).
- ²⁶ R. W. Walker, Gas Kinetics and Energy Transfer (Spec. Period. Rep., The Chemical Society, London, 1977), vol. 2, p. 296.
- ²⁷ E. L. Metcalfe and A. F. Trotman-Dickenson, J. Chem. Soc., 1960, 5072.
- ²⁸ R. J. Cvetanovic and R. S. Irwin, J. Chem. Phys., 1967, 46, 1694.
- ²⁹ J. A. Kerr and M. J. Parsonage, Evaluated Kinetic Data on Gas-Phase Addition Reactions (Butterworth, London, 1972).

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See facing page for Appendix 1.

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APPENDIX

FORMATION OF PRODUCTS FROM RADICALS A, B AND C

rad	ical → product	reaction sequence	initial yield (relative %) (mixture I)
	i-C ₃ H ₇ • i-C ₄ H ₈	(1A)	12
/	23DMB-1	(3A)	.2
radical A	02 DMB-2	(4A), (5A), (7A)	1
(сн ₃) ₂ ссн (сн ₃) ₂ –	$\frac{O_2}{O_2} \rightarrow TMO$	(4A), (5A), (6A)	2
L CH2 (17 ± 1%)	TMTHF	(4A), (9A), (10A)	0.2
	, t−C₄H ₉ "+ C₃H ₆	(1 B)	10
	33DMB-1	(4B), (6B), (10B) (3B)	negligible
radical B	02 TMTHF	(4B), (7B), (11B)	0.2
(CH ₃) ₃ CCH(CH ₃)CH ₂ (11 ± 1%) \	Oz 2-methyl-2-t-butyl- oxiran	(4B), (5B), (8B)	0 (not detected)
	TRIMB-1	(2B)	< 1
radical C	i-C ₄ H ₈ + i-C ₃ H ₇	(1C)	57
(CH ₃) ₃ CC(CH ₃) ₂	^O 2 → TRIMB-1	(2C)	14
(71 ± 2%)	DMB-2	(3C)	0.1