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Decomposition of 2,3-Dimethylbutane in the Presence of Oxygen

Part 1.—Thermochemistry of the Reaction $(CH_3)_2CHCH(CH_3)_2 \rightarrow 2i-C_3H_7$

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The decomposition of 2,3-dimethylbutane (DMB) in the presence of O_2 in KCl-coated vessels has been studied at 480, 500 and 540 °C over a wide range of mixture composition. At low pressures of O_2 the main initiation reaction is

$$(CH_3)_2 CHCH(CH_3)_2 \rightarrow 2i - C_3 H_7 \tag{10}$$

but the reaction

 $(CH_3)_2CHCH(CH_3)_2 + O_2 \rightarrow HO_2 + (CH_3)_2CHC(CH_3)_2$ (O)

becomes dominant at the higher pressures of O_2 used.

From measurements of the yield of propene, formed in 99% yield from i-C₃H₇ radicals, accurate values of k_{10} are obtained after extrapolation to zero O₂ and DMB pressures. Combination with Tsang's high-temperature results gives $\log_{10}(A_{10}/s^{-1}) = 16.42 \pm 0.10$ and $E_{10} = 319.1 \pm 1.5$ kJ mol⁻¹ over the temperature range 750–1200 K. These values are compared with parameters for similar systems and a simple relation has been developed to calculate the activation energy for C—C homolysis in alkanes and alkenes.

By use of the published values for k_{-10} , a value of $\Delta_{\rm f} H_{298}^{\circ}(i\text{-propyl}) = 79.6 \pm 2.0 \text{ kJ mol}^{-1}$ is obtained, which corresponds to $D_{298}^{\circ}(\text{CH}_3\text{-CHCH}_3\text{--H}) = 401.3 \pm 2.0 \text{ kJ mol}^{-1}$. With these values a self-consistent set of data is available for the heats of formation of the prototypical alkyl radicals, ethyl (117.0 ± 4.0 kJ mol^{-1}), i-propyl and t-butyl (37.6 ± 2.0 kJ mol^{-1}).

From measurements of the yield of but-2-ene in the initial stages of reaction, values of k_{12} of $(3.0\pm0.3)\times10^{-8}$ s⁻¹ at 480 °C and $(1.15\pm0.15)\times10^{-7}$ s⁻¹ at 500 °C are obtained for the reaction

$$(CH_3)_2 CHCH(CH_3)_2 \rightarrow (CH_3)_2 CHCHCH_3 + CH_3.$$
(12)

Arrhenius parameters of $\log_{10}(A_{12}/s^{-1}) = 16.6$ and $E_{12} = 348$ kJ mol⁻¹ are recommended.

Despite numerous studies, the heats of formation and entropies of the prototypical alkyl radicals ethyl, i-propyl and t-butyl remain uncertain.¹ The t-butyl radical has received most attention, and from a critical review of the literature McMillen and Golden¹ report that various 'reliable' techniques give values of $\Delta_f H_{298}$ (t-butyl) over the wide range from 31 to 48 kJ mol⁻¹. Values > ca. 40 kJ mol⁻¹ are inconsistent with currently 'accepted' $\Delta_f H_{298}$ values for ethyl and propyl radicals^{1, 2} and with a considerable body of other apparently reliable kinetic data. This inconsistency is illustrated in particular by the following points.

(i) Relatively large negative values of up to -12 kJ mol^{-1} are required for the activation energy of the reaction

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when calculated thermochemically from the activation energy of the reverse reaction, which appears to be known accurately.^{1,3}

(ii) The significant increase in the activation energy for the reactions of each of the selective radicals I, Br, H and CH₃ with the alkanes from i-butane to propane to ethane^{4, 5} implies a decrease in the C—H bond dissociation energy of 15 kJ mol⁻¹ from C_2H_5 —H to CH₃CHCH₃—H and of 12 kJ mol⁻¹ from CH₃CHCH₃—H to (CH₃)₃C—H.⁴ With a value of $\Delta_f H_{298}(t-C_4H_9) = 48$ kJ mol⁻¹, then the prototypical C—H bond dissociation energies in ethane, propane and i-butane become 426, 411 and 399, respectively, compared with values of 410, 397 and 389 kJ mol⁻¹ recommended by McMillen and Golden.¹ As the latter authors point out, such revisions of the individual values would have serious implications for current views on mechanistic organic chemistry and for a wide area of kinetics, so that there are compelling reasons for the determination of more reliable thermochemical data for the prototypical alkane systems.

Recently Baldwin *et al.*,² from a study of the decomposition of 2,2,3-trimethylbutane in the presence of O_2

$$(CH_3)_3CCH(CH_3)_2 \rightarrow t - C_4H_9 + i - C_3H_7 \tag{A}$$

obtained $\Delta_{\rm f} H_{298}(i\text{-propyl}) = 80.8 \text{ kJ mol}^{-1}$ and $D_{298}(\rm CH_3CHCH_3-H) = 402.5 \text{ kJ} \text{ mol}^{-1}$, but these values depend on the value taken (37.6 kJ mol}^{-1}) for $\Delta_{\rm f} H_{298}(t\text{-butyl})$. Pratt and Rogers have studied the pyrolysis of propane⁶ and of butane⁷ using a wall-less reactor and recommended $\Delta_{\rm f} H_{298}(\text{ethyl}) = 117 \text{ kJ mol}^{-1}$, in excellent agreement with a value of 116 kJ mol}^{-1} obtaind from an analysis of the $H + C_2H_6 \rightarrow C_2H_5 + H_2$ system.⁸

Although these values give sensible variations in the prototypical C—H bond dissociation energies in alkanes and the activation energy for the t-C₄H₉+HI reaction is no longer required to be negative, in view of the widespread relevance of these thermochemical aspects a further determination of the heat of formation of i-propyl radicals is warranted in a manner which is not dependent on $\Delta_f H_{298}$ (t-butyl).

Studies of the decomposition of the two strained alkanes tetramethylbutane⁸ (TMB) and trimethylbutane (TRIMB)² in the presence of O_2 in KCl-coated vessels have been very successful in giving Arrhenius parameters for the primary decomposition steps which have then been used to calculate heats of formation for the t-butyl and i-propyl radicals. For TMB decomposition, the basic mechanism involves the following reactions:

$$TMB \longrightarrow 2t - C_4 H_9 \tag{1}$$

$$t-C_4H_9+O_2 \longrightarrow i-C_4H_8+HO_2$$
(2)

$$HO_2 \xrightarrow{\text{surrace}} {}^{1}H_2O + {}^{3}H_2O \qquad (3)$$

$$2HO_2 \longrightarrow H_2O_2 + O_2 \tag{6}$$

$$H_2O_2 \xrightarrow{\text{surface}} H_2O + \frac{1}{2}O_2.$$
 (7)

The mechanism is complicated slightly by a small contribution from

$$HO_2 + TMB \rightarrow H_2O_2 + (CH_3)_3CC(CH_3)_2CH_2$$
(4)

* The reaction numbers used are consistent with previous publications.^{2,8}

and, at temperatures > ca. 450 °C, by the homogeneous decomposition of H₂O₂ and the subsequent reaction of TMB with the OH radicals produced:

$$H_{a}O_{a} + M \rightarrow 2OH + M$$
 (8)

$$OH + TMB \rightarrow H_2O + (CH_3)_3CC(CH_3)_2CH_2.$$
(9)

At least 95% of the $(CH_3)_3CC(CH_3)_2CH_2$ radicals decompose under the conditions used to give i-butene and t-butyl radicals.⁹ A very similar mechanism may be written for the decomposition of TRIMB, although it is further complicated by the presence in the alkane of the tertiary C—H bond, which results in a greater contribution to the rate of decomposition by radical chain processes.²

Although the density of CH_3 radicals in dimethylbutane (DMB) is lower than in TMB and TRIMB, the residual strain in the central C—C bond should markedly facilitate the decomposition of DMB into two i-propyl radicals:

$$\mathsf{DMB} \to 2\mathbf{i} \cdot \mathbf{C}_3 \mathbf{H}_7. \tag{10}$$

99% of i-C₃H₇ radicals will react with O_2 to give propene by¹⁰

$$i \cdot C_3 H_7 + O_2 \rightarrow C_3 H_6 + HO_2 \tag{11}$$

so that reactions (10), (11), (3), (6) and (7) form a basic mechanism for the decomposition of DMB, giving an overall stoichiometric equation in a KCl-coated vessel:

$$DMB + \frac{1}{2}O_2 \rightarrow 2C_3H_6 + H_2O.$$
 (s)

The simple relationships

$$\Delta[\text{DMB}] = \Delta_2^1[\text{C}_3\text{H}_6] = \frac{2}{3}\Delta P \tag{I}$$

should then apply and the rate of loss of DMB should be given by

$$-d[DMB]/dt = k_{10}[DMB].$$
(II)

Three factors complicate the basic mechanism. (i) The reaction of DMB with O_2

$$DMB + O_2 \rightarrow (CH_3)_2 CHC(CH_3)_2 + HO_2 \tag{O}$$

competes with the homolysis, reaction (10). No rate constant is available for reaction (O) but use¹¹ of $k_0 = 2.0 \times 10^{10} \exp(-183000 \text{ J mol}^{-1}/RT) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, where 183000 J mol⁻¹ is the endothermicity of reaction (O), together with^{2, 12} $k_{10} = 10^{16.5} \exp(-317000 \text{ J mol}^{-1}/RT) \text{ s}^{-1}$ gives rate₀/rate₁₀ = 0.45 at 500 °C and 30 Torr O₂. (ii) Owing to the presence of the two tertiary C—H bonds in DMB, radical attack by HO₂ will occur readily so that the chain contribution to the overall consumption of DMB will be considerably greater than the 10–20% observed with TMB. (iii) Two different species of alkyl radical are formed in radical attack on DMB, particularly by the non-selective OH radical, so that mechanistic paths are difficult to isolate.

A study of the decomposition of DMB in the presence of O_2 in KCl-coated vessels has been carried out over the temperature range 480–540 °C. As the main aim of this paper is the determination of the kinetic and thermochemical parameters associated with reaction (10), emphasis has been placed on the precise determination of k_{10} rather than a detailed product analysis over wide extents of reaction. Detailed studies of the decomposition of DMB have been carried out by Tsang¹² over the temperature range 1000–1200 K using a single-pulse shock tube and by Bull *et al.*,¹³ who studied the thermal pyrolysis over the range 667–770 K.



Fig. 1. [Propene] against time profiles for DMB + O_2 mixtures at 540 °C. DMB and O_2 pressures (Torr) as follows: \times , 0.5, 14.5; \bigcirc , 2, 13; \triangle , 5, 10; \bigtriangledown , 2, 28; \Box , 2, 58.

EXPERIMENTAL

Reactions were carried out in cylindrical Pyrex vessels, 20 cm in length and 5.2 cm i.d., freshly coated each week with potassium chloride. The mixtures of DMB and O_2 were pre-mixed prior to entry into the reaction vessel. Pressure changes and absolute pressures < 50 Torr were measured with a Southern Electronic SE 180 pressure transducer, capable of an output of 1 mV for a pressure change of 1 Torr in the reaction vessel. A microprocessor-controlled timing unit coupled to solenoid valves was used both to admit gases to the vessel and to take samples at pre-set times. As the response time of the valves was *ca*. 0.1 s, very precise admission and sampling times could be achieved. A Perkin–Elmer Sigma One microprocessor-operated gas chromatograph with very rapid integration facilities was used to determine the products, except for HCHO and CO. HCHO was estimated colorimetrically¹⁴ and CO was determined by use of a Carlo-Erba gas chromatograph which incorporated a helium ionisation detector. No analysis was made for H₂O, H₂O₂ or CO₂.

RESULTS

Experiments to determine the products have been carried out over a wide range of mixture composition at 480, 500 and 540 °C. Below 480 °C, the reaction becomes inconveniently slow with the possibility of surface effects and above 540 °C the decomposition of H_2O_2 becomes too rapid. Total pressures between 15 Torr, where reaction (10) is dominant, and 120 Torr, where reaction (O) is dominant, have been used with DMB pressures between 0.5 and 10 Torr, giving $[O_2]/DMB]$ ratios varying between 0.5 and 240. Attention has been focussed mainly on the initial yields of propene at various consumptions of DMB usually not exceeding 10%. Fig. 1 shows the concentration against time profiles for several mixtures at 540 °C. Propene is clearly formed in a primary process, but its profiles show autocatalysis, which increases in degree as both the total pressure and the pressure of DMB increase, almost certainly because of decomposition of the product H_2O_2 . Table 1 shows the other

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			CH₄	2MB2E	23DMB2E	E 23DMB1E	3MB1E	but-2-ene
T∕°C	DMB	$O_2/Torr$	C_3H_6	C ₃ H ₆	C ₃ H ₆	C ₃ H ₆	C_3H_6	C_3H_6
480	2	13	0.40	0.54	0.072	0.24	0.011	0.0039
	10	5	0.62	0.53	0.024	0.081	0.008	_
500	2	13	0.40	0.45	0.043	0.138	0.011	0.0041
	1	59	0.19	0.54	0.100	0.31	0.020	
	5	10	0.55	0.60	0.047	0.160	0.017	—
540	2	13	0.43	0.46	0.025	0.083	0.009	_
	2	58	0.29	0.55	0.055	0.085	0.014	
	5	10	0.56	0.61	0.021	0.064		

Table 1. Initial values of relative yields of products

initial products obtained for several of the mixtures used at 480, 500 and 540 °C. Under all conditions used, propene is the major product. In addition, large amounts of CH₄, 2-methylbut-2-ene (2MB2E) and 2,3-dimethylbut-1-ene (23DMB1E) are formed, together with smaller yields of 2,3-dimethylbut-2-ene (23DMB2E), 3-methylbut-1-ene (3MB1E) and but-2-ene. At the higher O₂ pressures used small amounts of oxygenated products such as tetramethyloxirane are observed as initial products and the yields of 23DMB1E and 23DMB2E increase markedly relative to those of the other products. Variation of the vessel diameter between 2.0 and 5.2 cm has no detectable effect on the results at low extents of reaction and low pressures of O₂, but slightly more autocatalysis is observed in the larger vessel later in the reaction and this effect is enhanced at high O₂ pressures. As seen from fig. 1, very reproducible results are obtained and it may be concluded that surface effects other than the destruction of HO₂ radicals and H₂O₂ are effectively absent.

DISCUSSION

FORMATION OF PRODUCTS

Apart from i- C_3H_7 radicals produced in reaction (10), three other radicals are formed from DMB. Loss of a CH₃ group gives the (CH₃)₂CHCHCH₃ radical, (A). The initiation reaction (O) and radical attack on DMB give the (CH₃)₂CCH(CH₃)₂ radical, (B), and radical attack also produces the alternative radical (CH₃)₂CHCH(CH₃)CH₂, (C). Likely reactions of these three radicals under the conditions used are shown in schemes 1–3.



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FORMATION OF BUT-2-ENE

The only simple mode of formation of but-2-ene is from the decomposition, reaction (13), of radical (A), which arises from the alternative homolysis, reaction (12), of DMB. However, radical (A) will also undergo the additional reactions (14)–(16) shown in scheme 1; alternative reactions such as the formation of other O-ring compounds will be considerable slower.¹⁵ The rate of formation of but-2-ene is then given by

$$\frac{d[but-2-ene]}{dt} = k_{12}[DMB] \left(\frac{k_{13}}{k_{13} + (k_{14} + k_{15} + k_{16})[O_2]} \right).$$
(i)

No experimental values are available for $k_{13}-k_{16}$, but patterns established recently for a number of alkyl radicals permit reasonable estimates to be made. Use of thermochemical data and Arrhenius parameters for the reverse reaction, reaction (-13),¹⁶ but with a modified² value of $\Delta_{\rm f} H_{298}[(\rm CH_3)_2\rm CHCHCH_3] = 30.7 \text{ kJ mol}^{-1}$, gives $A_{13} = 10^{14.0} \text{ s}^{-1}$ and $E_{13} = 130.4 \text{ kJ mol}^{-1}$, so that $k_{13} = 9.0 \times 10^4 \text{ s}^{-1}$ at 480 °C in very good agreement with rate constants for similar decompositions.¹⁷



Fig. 2. Plots of k_{12}^{obs} against time for DMB+O₂ mixtures. DMB and O₂ pressures (Torr) as follows: \bigcirc , 2, 13; \times , 1, 14; \triangle , 0.75, 14.25; \bigcirc , 0.5, 14.5.

For a range of reactions similar to reactions (14) and (15), Baldwin *et al.*¹⁸ give $\log_{10} (k/\text{dm}^3 \text{ mol}^{-1} \text{s}^{-1}) = 5.09-0.0411\Delta H/\text{kJ mol}^{-1}$ per C—H bond at 480 °C,* where the units of ΔH are kJ mol⁻¹, and $E_{14} = E_{15} = 20$ kJ mol⁻¹ is recommended.^{20, 21} Reaction (16) proceeds through the equilibrated $R + O_2 \rightleftharpoons RO_2$ step (K_R) followed by a 1,4t H-atom transfer ($k_{1,4t}$) and by decomposition,¹⁵ so that $k_{16} = K_R k_{1,4t}$. Use of Benson's²² thermochemical data to calculate $K_R = 219$ dm³ mol⁻¹ at 480 °C, and $k_{1,4t}^{15} = 1.83 \times 10^5 \text{ s}^{-1}$ gives $k_{16} = 4.0 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ with^{11,15} $E_{16} = -4$ kJ mol⁻¹. With these parameters and 15 Torr O₂, 91, 79 and 70% of radical (A) forms but-2-ene at 540, 500 and 480 °C, respectively, falling to 33% with 120 Torr O₂ at 500 °C and 71% with 60 Torr O₂ at 540 °C.

As the ratio [2MB2E]/[but-2-ene] is ca. 100, it is concluded that negligible amounts of 2MB2E are formed from radical (A) at 15 Torr O₂ and that < 1% of the total 2MB2E is formed from radical (A) even at the highest O₂ pressure used. However, as the ratio [3MB1E]/[but-2-ene] ≈ 5 , significant proportions of 3MB1E are formed from radical (A).

Fig. 2 shows a plot of k_{12}^{obs} against time for different mixtures at 15 Torr total pressure and 500 °C, where k_{12}^{obs} is defined by

$$\Delta[\text{but-2-ene}]/\Delta t = k_{12}^{\text{obs}}[\text{DMB}].$$
 (ii)

The apparent increase in k_{12}^{obs} both with time and [DMB] is almost certainly caused by interference with the but-2-ene signal from the gas chromatograph by that from the secondary product acetaldehyde. Formation of but-2-ene in secondary processes also occurs. At 540 °C and at pressures > 15 Torr, the interference is marked even in the early stages of reaction. From the plot, $k_{12}^{obs} = (9.0 \pm 1.0) \times 10^{-8} \text{ s}^{-1}$, which on application of eqn (i) gives $k_{12} = (1.15 \pm 0.15) \times 10^{-7} \text{ s}^{-1}$ at 500 °C. At 480 °C, use of the results at 15 Torr gives $k_{12} = (3.0 \pm 0.3) \times 10^{-8} \text{ s}^{-1}$. These values will be discussed later.

* The original equation has been modified¹⁹ because $\Delta_r H_{298}(HO_2)$ has been reduced from 21 to 10.5 kJ mol⁻¹.



Fig. 3. Plots of k_{obs} against time for mixtures at 15 Torr total pressure. DMB and O₂ pressures (Torr) as follows: ○, 2, 13; ×, 1.5, 13.5; □, 1, 14; △, 0.75, 14.25; ●, 0.5, 14.5.

RATE CONSTANT FOR REACTION (10)

In the absence of a chain contribution to the overall formation of propene, then k_{10} may be obtained from

$$d[C_{3}H_{6}]/dt = (1.98k_{10} + 1.99k_{0}[O_{2}]f)[DMB] = k_{app}[DMB]$$
(iii)

where the factors 1.98 and 1.99 arise because 99% of i-C₃H₇ radicals react with O₂ to give propene and 1% give propene oxide, ¹⁰ and f is the fraction of $(CH_3)_2CCH(CH_3)_2$ radicals, formed in reaction (O), that give propene by reaction (18). Use of the initial value of $d[C_3H_6]/dt[DMB]$ should give k_{app} for any particular value of $[O_2]$ since the value of f will also be constant. In practice, a higher value of the rate constant, k_{obs} , is obtained because of the pronounced chain contribution to the overall rate of formation of propene, particularly at high pressures of DMB and of O₂. The following procedure was adopted to determine values of k_{10} . First, $\Delta [C_3H_6]/\Delta t[DMB]$ was plotted against time over the first 5-10% reaction and extrapolated to zero time to obtain k_{obs}° for any single mixture; fig. 3 shows a series of these plots at 500 °C. Secondly, for constant $[O_2]$, the values of k_{obs}° were plotted against [DMB] to obtain $k_{\rm app}$, which is effectively the rate constant for removal of DMB in the initiation reactions (10) and (O) only. Fig. 4 shows the plots obtained for the four different series of O₂ mixtures used at 500 °C. In practice, at any particular total pressure, the pressure of O₂ does rise very slightly as the value of [DMB] is reduced. However, the value of the intercept is not affected and is obtained for a pressure of O₂ equal to the total pressure of the mixture as the pressure of DMB is reduced to zero. Finally, fig. 5 shows a plot of k_{app} against [O₂], and as shown by eqn (iii) the value of k_{10} is given by the intercept. The gradient is related to the rate constant for reaction (O) but will not be discussed further here. Results at 540 °C were treated similarly, and the plot of k_{app} against $[O_2]$ is also shown in fig. 5. Values of $k_{10} = (8.1 \pm 0.4) \times 10^{-5}$ and

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Fig. 4. Plot of k_{obs}° against [DMB] at 500 °C for various total pressures (Torr) of DMB+O₂: \triangle , 120; \Box , 60; \bigcirc , 30; \times , 15.



Fig. 5. Plots of k_{app} against [O₂]: \bigcirc , 540 °C (1.h. scale); ×, 500 °C (r.h. scale).

 $(7.2\pm0.4)\times10^{-6}$ s⁻¹ were obtained from the plots at 540 and 500 °C, respectively. At 480 °C results were only obtained at a total pressure of 15 Torr, and a value of $k_{10} = (1.98\pm0.09)\times10^{-6}$ s⁻¹ was determined by 'correcting' k_{app} for the small contribution from k_0 , based on the conclusions reached at 500 and 540 °C. As the correction amounts to *ca*. 20% of the value of k_{10} an accurate value is obtained.



Fig. 6. Arrhenius plot for k_{10} : \triangle , this work; \bigcirc , Tsang,¹² original results modified as in text.

ARRHENIUS PARAMETERS AND THERMOCHEMISTRY OF REACTION (10)

Studies above 540 °C are inadvisable because of the degree of autocatalysis even at low pressures because of the decomposition of H_2O_2 , and below 480 °C the reaction rate becomes extremely slow so that surface effects may interfere. The values of k_{10} give $A_{10} = 10^{15.5 \pm 1.0} \text{ s}^{-1}$ and $E_{10} = 305 \pm 15 \text{ kJ mol}^{-1}$. However, to obtain more accurate Arrhenius parameters the present results have been combined with those obtained by Tsang,¹² who studied reaction (10) using a single-pulse shock tube over the temperature range 1000–1200 K. Tsang gives $A_{10} = 10^{16.1}$ and $E_{10} = 318 \text{ kJ mol}^{-1}$, based on the use of the decyclisation of cyclohexene as a reference reaction. As shown earlier, because of more recent work the Arrhenius parameters of the reference reaction have been modified slightly, so that Tsang's results now give $k_{10} = 0.59$ at 1000 K and 334 s^{-1} at 1200 K compared with his original values of 0.32 and 186 s⁻¹, respectively. The revised values are plotted in Arrhenius form in fig. 6, together with the present results, and an excellent line may be drawn through the points. Linear regression gives $\log_{10} (A_{10}/\text{s}^{-1}) = 16.42 \pm 0.10$ and $E_{10} = 319.1 \pm 1.5 \text{ kJ mol}^{-1}$.

Bull *et al.*¹³ studied the pyrolysis of DMB over the ranges 667–770 K and 10–180 Torr and were able to account for the product formation by use of a very comprehensive mechanism. By equating the initiation and termination rates, they were able to determine the composite term $(k_{10}+k_{12})$. The values of $(k_{10}+k_{12})$ increased significantly with pressure and they obtained infinite-pressure values from the intercepts of plots of $1/(k_{10}+k_{12})$ against 1/[DMB]. Although they give Arrhenius parameters for the combined initiation of $A = 10^{17.1}$ s⁻¹ and E = 329 kJ mol⁻¹, which are relatively close to the present values, the complexity of the system and the approximate nature of the extrapolation to high pressures suggests some uncertainty in the rate constants. This is consistent with the view of Bull *et al.*, who preferred to calculate the Arrhenius parameters for reaction (10) thermochemically.

The present values for reaction (10) are compared in table 2 with Arrhenius

reaction	$\log{(A/\mathrm{s}^{-1})}$	$E/kJ mol^{-1}$	strain/group /kJ mol ⁻¹	T range/K	ref.
$C_2H_6 \rightarrow 2CH_3$	16.7	372.3	0	600-1000	23
$C_4H_{10} \rightarrow 2C_2H_5$	16.4	343.5	14.4	900-1200	23
$C_6H_{14} \rightarrow 2n-C_3H_7$	16.5	342.7	14.8	600-1000	23
$DMB \rightarrow 2i-C_3H_7$	16.42	319.1	26.6	750-1200	this work
$(s-C_4H_9)_2 \rightarrow 2s-C_4H_9$	16.3	316.0	28.2	1000-1200	a
$(t-C_4H_9)_2 \rightarrow 2t-C_4H_9$	16.78	290.4	41.0	710-1140	8
$(C_3H_5)_2 \rightarrow 2C_3H_5$	14.4	248.5	61.9 ^b	600-1000	23
$(C_4H_7)_2 \rightarrow 2C_4H_7$	15.8	236.8	67.8°	600-1000	23

Table 2. Arrhenius parameters for symmetrical homolysis in hydrocarbons

^a W. Tsang, J. Chem. Phys., 1972 76, 143. ^b Includes delocalisation effect.

parameters for the symmetrical homolysis of other alkanes and of two dienes. The fall in activation energy from ethane to tetramethylbutane is closely related to the degree of strain in the central C—C bond, and the further reduction for the dienes arises from the stabilisation of the alkenyl radicals produced through electron delocalisation. A strain factor may be calculated for each alkyl or alkenyl group* by arbitrarily assuming zero strain in ethane; the values are given in table 2. If the strain assigned to each group is independent of any other group to which it is joined, then the activation energy for any C—C homolysis may be calculated from

$$E_{\mathbf{R}-\mathbf{R}'} = (E_{\mathbf{R}-\mathbf{R}} + E_{\mathbf{R}'-\mathbf{R}'})/2$$

$$\mathbf{R}-\mathbf{R} \to 2\mathbf{R}, \quad E_{\mathbf{R}-\mathbf{R}}$$

$$\mathbf{R}-\mathbf{R}' \to \mathbf{R} + \mathbf{R}', \quad E_{\mathbf{R}-\mathbf{R}'}$$

$$\mathbf{R}'-\mathbf{R}' \to 2\mathbf{R}', \quad E_{\mathbf{D}',\mathbf{R}'}$$
(iv)

The application of this very simple relationship is shown in table 3 for values of activation energies between 245 and 355 kJ mol⁻¹. Extremely good agreement is observed with the few experimental values available, even allowing only ± 4 kJ mol⁻¹ for experimental error. Excellent agreement is also obtained with values recommended by Allera and Shaw²³ in a recent review. As table 2 shows, the strain energies associated with the C₂H₅ and n-C₃H₇ groups are virtually indistinguishable, as are those for the i-C₃H₇ and s-C₄H₉ groups. Assignments for radicals not included in table 2 should be possible without serious error. Thus, n-C₄H₉, n-C₅H₁₁ and i-C₄H₉ are assigned strain energies of 15 kJ mol⁻¹ and secondary radicals such as CH₃CHCH(CH₃)₂ will have a strain factor of 28 kJ mol⁻¹. A value of E = 357.5 kJ mol⁻¹ is predicted for the dissociation of pentane into CH₃+n-C₄H₉, in excellent agreement with the recommended²³ value of 357.3 kJ mol⁻¹.

As indicated in table 2, a value of $10^{16.5\pm0.2}$ s⁻¹ for the A factor appears applicable to symmetrical C—C homolysis in alkanes, and allowance may be made for path degeneracy and for electron delocalisation where alkenyl radicals are formed. It is probable, therefore, that both the A and E values can be simply estimated as indicated with sufficient accuracy for the C—C homolysis of alkanes and alkenes to permit the

^{*} The strain factor includes the delocalisation energy for alkenyl radicals and may of course involve other factors in addition.

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	E/kJ			
reaction	calc.	obs.	ref.	
$C_3H_8 \rightarrow Me + Et$	357.9	356.1	23	
$n-C_4H_{10} \rightarrow Me+n-Pr$	357.6	358.6	23	
$i-C_4H_{10} \rightarrow Me+i-Pr$	345.7	343.1 ^a	23	
$(CH_3)_2CHCH_2CH_3 \rightarrow Me + s-Bu$	347.9	344.2	23	
$n-C_5H_{12} \rightarrow Et + n-Pr$	343.2	342.7	23	
$(CH_3)_2CHCH_2CH_3 \rightarrow Et + i-Pr$	331.3	331.4	23	
$(CH_3)_4 C \rightarrow CH_3 + t - Bu$	331.4	326.5 ^a	3	
$(CH_3)_3CCH(CH_3)_3 \rightarrow t-Bu+i-Pr$	304.7	305.1ª	3	
$(CH_3)_3CCH(CH_3)CH_2CH_3 \rightarrow t-Bu+s-Bu$	303.2	302.0 ^a	ь	
$1 - C_4 H_8 \rightarrow Me + C_8 H_5$	310.5	307.5 ^a	23	
$2 - C_5 H_{10} \rightarrow Me + C_4 H_7$	304.6	305.4	23	
$I - C_5 H_{10} \rightarrow Et + C_3 H_5$	296.1	298.7	23	
$1 - C_6 H_{12} \rightarrow n - Pr + C_3 H_5$	295.7	297.4	23	
$2 - C_7 H_{14} \rightarrow i - Pr + C_4 H_7$	289.8	289.9	23	
$(CH_3)_3CCH_2CH=CH_3 \rightarrow t-Bu+C_3H_5$	269.5	275.0 ^a	c	
$CH_{3} = CHCH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}H_{3} + C_{4}H_{3}$	242.7	245.6	23	

Table 3. Observed	land	calculated	activation	energies for	r C(🗅 homolysis	in hydrocarbons
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^a Experimentally determined values. ^b W. Tsang, J. Phys. Chem., 1972, 76, 143. ^c W. Tsang, J. Chem. Phys., 1967, 46, 2817.

calculation of rate constants, which are accurate to better than a factor of 2 over the temperature range 700-1200 K.

The agreement between the calculated and observed values of the activation energy for the homolyses emphasises that a large body of self-consistent data is available. The agreement also adds support to the view that in alkanes the bond dissociation energies for primary, secondary and tertiary C—H bonds may be taken as $D(C_2H_5$ —H), $D(i-C_3H_7$ —H) and $D(t-C_4H_9$ —H), respectively. Although eqn (iv) should give the same values of E as those obtained from the heats of formation of the radicals involved, it effectively bypasses a number of uncertain steps in the calculation. As the observed values of the activation energies were obtained in the range 700–1200 K, eqn (iv) should be reliable over this range for other reactions not included in table 3.

Thermochemical quantities may be obtained for the i-C₃H₇ radical by combination of the values for k_{10} and k_{-10} . Parkes and Quinn²⁴ suggest a small negative temperature coefficient with $k_{-10} = (4.8 \pm 1.2) (T/300)^{-\frac{1}{2}} \times 10^9$ dm³ mol s⁻¹, whereas Arrowsmith and Kirsch²⁵ find a small positive temperature coefficient between 301 and 424 K with $k_{-10} = 8.4 \times 10^9$ exp (-1340 J mol⁻¹/RT) dm³ mol⁻¹ s⁻¹. In both studies the trend with temperature is barely significant compared with experimental error. More recently, Arthur and Anastasi,²⁶ using molecular modulation spectroscopy as in the two previous studies, give $k_{-10} = 5.96 \times 10^9$ at 308 K. The evidence for a temperature coefficient is contradictory, and in any event its magnitude is extremely small, so $E_{-10} = 0$ will be assumed. The mean value of k_{-10} from the three studies over the range 301-424 K is $(5.25\pm0.35) \times 10^9$ dm³ mol⁻¹ s⁻¹. With $E_{-10} = 0$, the enthalpy change $\Delta H_{926}(10)$ of reaction (10) at 926 K, corresponding to the mean value of 1/T for the present work and Tsang's study, is given by $\Delta H_{926}(10) = E_{10} + RT$, from which $\Delta H_{926}(10) = 326.8 \pm 1.5$ kJ mol⁻¹. With the published²⁷ value of $\Delta_f H_{926}(DMB) =$

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	$C_p/\mathrm{J}~\mathrm{mol^{-1}}~\mathrm{K^{-1}}$			$\Delta H_T(10)$	$\Delta S_T(10)$
T/K	DMB	i-C ₃ H ₇	$/\text{Jmol}^{-1}\text{K}^{-1}$	$/kJ \text{ mol}^{-1}$	$/J \text{ mol}^{-1} \text{ K}^{-1}$
298	139.4	73.2	+7.0		
400	181.7	89.5	-2.7	+0.22	+0.63
500	218.4	103.8	-10.8	-0.46	-0.88
600	250.2	118.0	-14.2	-1.71	-3.16
800	301.7	140.2	-21.3	- 5.36	-8.27
926				-8.20	-11.5
1000	340.6	158.2	-24.2		

Table 4. Changes in the value of $\Delta H(10)$ and $\Delta S(10)$ with temperature

 $\Delta H_{298}(10) = 326.8 + 8.2 = 335.0 \text{ kJ mol}^{-1}$ $\Delta S_{298}(10) = 172.4 + 11.5 = 183.9 \text{ J K}^{-1} \text{ mol}^{-1}$

Table 5. Heats of formation of alkyl radicals

R	$\Delta_{\rm f} H^{\ominus}_{298}({ m R})/{ m kJ} \ { m mol}^{-1}$	$D_{298}^{\ominus}(\mathrm{R-H})/\mathrm{kJ} \mathrm{mol}^{-1}$
CH ₃	145.6±1.0	438.4±1.0
C ₂ H ₅	117.0 ± 4.0	419.5 ± 4.0
i-C ₃ H ₇	79.6 ± 2.0	401.3 ± 2.0
i-C ₄ H ₉	37.6 ± 2.0	390.2 ± 2.0

 -211.3 ± 1.0 , then $\Delta_{\rm f} H_{926}(\rm i-C_3H_7) = 57.8 \pm 1.3 \text{ kJ mol}^{-1}$, which corresponds to $D(\rm i-C_3H_7-H) = 404.2 \text{ kJ mol}^{-1}$. From $\log_{10} (K_{10}/\text{atmosphere}) = -9.472$ at 926 K, $\Delta G_{926}^{\odot}(10) = 167.9 \text{ kJ mol}^{-1}$, which in combination with $\Delta H_{926}(10)$ gives $\Delta S_{926}^{\odot}(10) = 172.4 \text{ J K}^{-1} \text{ mol}^{-1}$. With $S_{926}^{\odot}(\text{DMB}) = 626.3$, then $S_{926}^{\odot}(\rm i-C_3H_7) = 399.0 \text{ J K}^{-1} \text{ mol}^{-1}$. This value is slightly below $S_{926}^{\odot}(C_3H_8)^{27} = 403.5 \text{ J K}^{-1} \text{ mol}^{-1}$, whereas a value 5-10 J K⁻¹ mol⁻¹ greater might be expected. However, the difference is well within the uncertainty involved in the calculations and in the long extrapolation of k_{-10} to 926 K from the experimental determinations below 400 K.

Conversion of the thermochemical values for the i- C_3H_7 radical from 926 to 298 K has been carried out with an assumed internal rotational energy barrier in the radical of 8.5 kJ mol⁻¹, as suggested earlier.^{8,28} The calculations are summarised in table 4 and give $\Delta H_{298}^{\odot}(10) = 335.0 \pm 2.5$ kJ mol⁻¹ and $\Delta S_{298}^{\odot}(10) = 183.9$ J K⁻¹ mol⁻¹. With²⁷ $\Delta_f H_{298}^{\odot}$ (DMB) = -175.9 ± 1.0 kJ mol⁻¹ and $S_{298}^{\odot}(DMB) = 365.8$ J K⁻¹ mol⁻¹, then $\Delta_f H_{298}^{\odot}$ i- $C_3H_7 = 79.6 \pm 1.8$ kJ mol⁻¹ and S_{298}^{\odot} (i- C_3H_7) = 274.9 J K⁻¹ mol⁻¹. The enthalpy value is extremely close to the value of 80.8 ± 4.0 kJ mol⁻¹ obtained from the trimethylbutane decomposition study² and the entropy may be compared with an estimated²⁹ value of 280.3 and with $S_{298}^{\odot}(C_3H_8) = 270.0$ J K⁻¹ mol⁻¹.

Table 5 summarises the thermochemical values for the i- C_3H_7 radical, together with those for the other prototypical radicals. The enthalpy values for i- C_3H_7 and t- C_4H_9 are consistent with the higher values suggested recently⁶⁻⁸ for $\Delta_r H_{298}^{\ominus}(C_2H_5)$ and $D(C_2H_5$ —H). The enthalpies of formation and bond-dissociation energies form a self-consistent set of data; the differences in the bond-dissociation energies are consistent with the observed differences in the activation energies for radical attack

k_{12}/s^{-1}	T/K	ref.
3.8×10^{-7}	750	13
3.0×10^{-8}	753	this work
1.15×10^{-7}	773	this work
1.41×10^{-2a}	1000	12
$1.22 \times 10^{-1 a}$	1200	12

Table 6. S	ummary of	`val	lues	of I	k_{12}
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^{*a*} Tsang's values modified as for k_{10} , see text.

on the prototypical alkanes.⁴ The value of $\Delta_f H_{298}^{\circ}(t-C_4H_9)$ is in excellent agreement with a value of 38.5 kJ mol⁻¹ obtained recently by Bracey and Walsh and quoted by Rossi and Golden.³⁰

RATE CONSTANT FOR REACTION (12)

Both Tsang¹² and Bull *et al.*¹³ report values for k_{12} obtained by measurement of the yield of but-2-ene (see table 6). The value of Bull *et al.* at 750 K is approximately a factor 4 higher than the present determination at 753 K and approximately a factor 4 higher than a value extrapolated from Tsang's high-temperature results. The latter discrepancy convinced Bull *et al.* that in their system but-2-ene was formed mainly in secondary processes. This conclusion is in agreement with the present observation that high values of k_{12} are obtained unless the but-2-ene is measured very early in the reaction. An Arrhenius plot of Tsang's results and the present values gives a good line but unlikely Arrhenius parameters of $A_{12} = 10^{18.5} \, \text{s}^{-1}$ and $E_{12} = 374 \, \text{kJ} \, \text{mol}^{-1}1$. Reference to tables 2 and 3 provides strong evidence that both are too high and it seems likely that Tsang has also overestimated k_{12} . Probably the most reliable Arrhenius parameters for reaction (12) are obtained using eqn (iv), which gives $E_{12} = 348 \, \text{kJ} \, \text{mol}^{-1}$, and values of $\log_{10} (A_{12}/\text{s}^{-1}) = 16.57 \, \text{and} \, 16.61$ are then obtained from k_{12} at 500 and 480 °C, respectively (vide supra). These values are clearly in excellent agreement with the A factors of other homolyses shown in table 2.

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