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The Decomposition of 2,2,3,3-Tetramethylbutane in KCland B_2O_3 -coated Vessels in the Presence of Oxygen

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The decomposition of 2,2,3,3-tetramethylbutane (TMB) in the presence of oxygen has been studied in both KCl-coated and aged boric-acid-coated vessels. The values for k_1 obtained with the two types of vessel surface are in close agreement, and combination of the values over the range 400-542 °C gives $A_1 = 1.04 \times 10^{17} \text{ s}^{-1}$, $E_1 = 294.7 \pm 3 \text{ kJ mol}^{-1}$, effectively identical with previous values using KCl-coated vessels, and thus confirming the thermochemistry suggested for the t-butyl radical:

$$(CH_3)_3C \longrightarrow C(CH_3)_3 \rightarrow 2(CH_3)_3C. \tag{1}$$

The observed rate constant, k_{obs} , defined by the equation

 $-d [TMB]/dt = k_{obs}[TMB]$

increases with increasing TMB concentration with both types of vessel surface and this variation has been used to evaluate the ratio $k_4/k_7^{\frac{1}{2}}$. The results with both types of vessel surface are in agreement, giving $A_4/A_7^{\frac{1}{2}} = 4.4 \times 10^5 \text{ (dm}^3 \text{ mol}^{-1} \text{ s}^{-1})^{\frac{1}{2}}$, $E_4 - \frac{1}{2}E_7 = 81.7 \pm 8 \text{ kJ mol}^{-1}$ over the range 400-520 °C:

$$HO_2 + (CH_3)_3C - C(CH_3)_3 \rightarrow H_2O_2 + (CH_3)_3C \rightarrow C(CH_3)_2CH_2$$
(4)

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2. \tag{7}$$

Previous papers¹⁻³ on the decomposition of 2,2,3,3-tetramethylbutane (TMB) in the presence of O_2 have concentrated on the evaluation of the Arrhenius parameters for reaction (1) and on the use of the system to study the reactions of t-butyl radicals¹ with H_2 , D_2 and O_2 , and to evaluate their entropy and enthalpy of formation.² In KCl-coated vessels, where HO₂ radicals are efficiently destroyed at the vessel surface, the basic mechanism involves reactions (1)-(3), and gives the rate expression (i)

$$-d [TMB]/dt = k_1 [TMB].$$
(i)

However, the observed rate constant increases² both with increasing concentration of TMB and with addition of inert gas. This is caused by two contributions to a very short chain, from HO₂ radicals through reaction (4), which competes with reaction (3), and reaction (5), and from OH radicals through reactions (8), (9) and (5), the H₂O₂ being formed by reactions (4) and (7) and being predominantly destroyed by the surface process (6). Reaction (10) also occurs to a very minor extent with $k_{10}/k_2 \approx 0.01$; Arrhenius parameters for this reaction have been given.

$$(CH_3)_3 C - C(CH_3)_3 \rightarrow 2t - C_4 H_9 \tag{1}$$

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

$$HO_2 \rightarrow \frac{1}{2}H_2O + \frac{3}{4}O_2$$
(3)

$$HO_2 + (CH_3)_3 CC(CH_3)_3 \rightarrow H_2O_2 + (CH_3)_3 CC(CH_3)_2 CH_2$$

$$\tag{4}$$

1166

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DECOMPOSITION OF 2,2,3,3-TETRAMETHYLBUTANE

$$H_{3})_{3}CC(CH_{3})_{2}CH_{2} \rightarrow i-C_{4}H_{8} + t-C_{4}H_{9}$$
^{surface}
(5)

$$H_{2}O_{2} \rightarrow H_{2}O + \frac{1}{2}O_{2} \tag{6}$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{7}$$

$$H_2O_2 + M \to 2OH + M \tag{8}$$

$$OH + (CH_3)_3 CC(CH_3)_3 \rightarrow H_2O + (CH_3)_3 CC(CH_3)_2 CH_2$$
(9)

$$t-C_4H_9+O_2 \to C_4H_8O+OH. \tag{10}$$

The present paper uses the variation of the observed rate constant in eqn (i) with TMB concentration in both KCl-coated and aged boric-acid-coated vessels to evaluate the rate constant k_4 .

EXPERIMENTAL

Reactions were carried out in cylindrical Pyrex vessels, 20 cm in length and 5.1 cm diameter. KCl-coatings were renewed every week, as previous studies² have shown that the efficiency of the surface for destruction of HO₂ and of H₂O₂ decreased markedly with older coatings. Aged boric-acid coatings were prepared as previously described.⁴ Studies were made over the range 400-520 °C in boric-acid-coated vessels but restricted to 420-470 °C in KCl-coated vessels. A wide range of mixture compositions (0.1-4.0 Torr TMB) was examined. The reaction was followed by using gas chromatography to measure the isobutene formed. Electromagnetic valves (opening and closing time < 0.1 s) were used with reaction times below 100 s to admit the gases from the mixing bulb into the reaction vessel, and to admit the reactants into the sampling bulb after a pre-determined time interval. To avoid complications resulting from reactions of isobutene, which become noticeable beyond 10% reaction, consumption of TMB was restricted to a maximum of 5% for those points used to elucidate rate constants. The time for 5% consumption varied from *ca*. 10 s at 520 °C to *ca*. 3000 s at 400 °C.

RESULTS AND DISCUSSION

KCl-COATED VESSELS

If H_2O_2 is always destroyed by reaction (6), and if the minor reaction (10) is ignored, the rate of reaction is given by eqn (ii) if reaction (3) is the sole termination process, and by eqn (iii) if reaction (7) is the sole termination process:

$$-d[TMB]/dt = k_1[TMB] + 2k_1k_4[TMB]^2/k_3$$
(ii)

$$-d[TMB]/dt = k_1[TMB] + k_4(k_1/k_7)^{\frac{1}{2}}[TMB]^{\frac{3}{2}}.$$
 (iii)

If reaction (3) is the sole termination process, the chain length increases with increasing temperature, since $E_4 \approx 80 \text{ kJ mol}^{-1}$, with increasing TMB concentration, and with inert gas addition (since k_3 is diffusion-controlled). If reaction (7) is the sole termination process, the chain length increases with TMB concentration, is independent of inert gas and decreases as the temperature increases, since E_1 (ca. 290 kJ mol⁻¹) > $2E_4$. Increase in temperature, in TMB concentration of addition of inert gas increases the HO₂ concentration and thus favours reaction (7) relative to reactions (3) and (4). Use of preliminary values² of k_1 and $k_4/k_7^{\frac{1}{2}}$ gives the percentage reaction due to the HO₂ chain for a mixture containing 2 Torr TMB+30 Torr O₂ at pressures of 60 and 500 Torr (N₂ addition) shown in table 1 for a range of temperature. At 60 Torr, the percentage increases and then decreases at high temperatures. This is because the second-order radical-radical reaction (7) increases in importance relative to the

R. R. BALDWIN, M. W. M. HISHAM, A. KEEN AND R. W. WALKER 1167

first-order processes (3) and (4) as the temperature increases, due to the increased HO_2 concentration resulting from the increased rate of dissociation of TMB.

Table 1 shows that the HO₂ chain contribution is small, and has its highest value in the range 400-470 °C. A further difficulty in using this small chain contribution to evaluate k_4 is that the OH chain becomes increasingly important as the temperature increases above *ca.* 450 °C; 2% of the total OH chain is due to reaction (10), with $k_{10}/k_2 \approx 0.01$, the remainder being due to the formation and decomposition of H₂O₂.

		chain reaction (%)					
	<i>T/</i> °C	HO ₂	chain	OH chain			
		at 60 Torr	at 500 Torr	at 60 Torr	at 500 Torr		
	400	7	31	2	2		
	440	12	29	2	6		
	470	16	24	3	16		
	500	12	12	5	31		
	540	9	5	14	60		

TABLE 1.—VARIATION OF CHAIN LENGTH WITH PRESSURE AND TEMPERATURE

To evaluate k_4 from the isobutene (IBE) against time curves, a computer treatment was used. It is convenient to express the HO₂ radical concentration in terms of the parameter $G = k_7^{\frac{1}{2}}[HO_2]$, since it is the ratio $R_4 = k_4/k_7^{\frac{1}{2}}$ that is actually involved in the computer treatment. Similarly k_3 enters as the ratio $R_3 = k_3/k_7^{\frac{1}{2}}$. The differential equations for TMB, H₂O₂, O₂, IBE, isobutene oxide (IBO) and H₂O are given by eqn (iv)-(ix), and the stationary-state equations for HO₂, OH and t-C₄H₉ radicals are given by eqn (x)-(xii), respectively:

$$-d[TMB]/dt = k_1[TMB] + R_4G[TMB] + k_9[OH][TMB]$$
(iv)

$$d[H_2O_2]/dt = G^2 + R_4 G[TMB] - k_6[H_2O_2] - k_8[M][H_2O_2]$$
(v)

$$-d[O_2]/dt = (k_2 + k_{10})(t - C_4H_9][O_2] - 0.75R_3G - 0.5k_6[H_2O_2] - G^2$$
(vi)

$$d[IBE]/dt = k_2[t-C_4H_9][O_2] + R_4G[TMB] + k_9[OH][TMB]$$
(vii)

$$d[IBO]/dt = k_{10}[t-C_4H_9][O_2]$$
(viii)

$$d[H_2O]/dt = k_8[H_2O_2] + 0.5R_3G + k_8[OH][TMB]$$
(ix)

$$2k_1[\text{TMB}] + 2k_8[\text{M}][\text{H}_2\text{O}_2] = 2G^2 + R_3G$$
(x)

$$2k_{8}[M][H_{2}O_{2}] + k_{10}[t - C_{4}H_{9}][O_{2}] = k_{9}[OH][TMB]$$
(xi)

$$2k_{1}[\text{TMB}] + R_{4}G[\text{TMB}] + k_{9}[\text{OH}][\text{TMB}] = (k_{2} + k_{10})[\text{t-}C_{4}H_{9}][\text{O}_{2}]. \quad \text{(xii)}$$

G is obtained from eqn (x), and eqn (xi) and (xii) then give $[t-C_4H_9]$ and [OH]. Eqn (iv)-(ix) are solved by the Kutta-Runge numerical integration method. H_2O_2 rapidly reaches a quasi-stationary value, so that computer time can be considerably reduced by using a short time step until the H_2O_2 is close to its quasi-stationary value, after which a stationary state is written for H_2O_2 with a much bigger time step.

Operation of the computer program requires values of the parameters k_1 , k_{10}/k_2 , R_3 , R_4 , k_6 and k_8 . The yield of IBE at various times is calculated for a range of mixtures

and compared with the experimental values. An optimisation procedure adjusts the parameters k_1 and R_4 so as to obtain minimum r.m.s. deviation. Reaction (10) plays only a very minor part, and the ratio $k_{10}/k_2 = 0.01$ obtained from previous studies³ of the IBO yield is sufficiently accurate. k_8 is known from direct studies^{5, 6} of the homogeneous decomposition of H_2O_2 . The values of k_3 and k_6 depend on the efficiency of the surface for destruction of HO_2 and H_2O_2 , respectively. In general, the surface destruction constant k_8 for a cylindrical vessel is given⁷ by eqn (xiii)

$$k_{\rm s} = aA_0/P(1+4aB/P) \tag{xiii}$$

where $A_0 = 32D_0^A/d^2$, $B = 8D_0^A/\epsilon \bar{c} d$. D_0^A is the diffusion constant of the species in gas A at unit pressure, ϵ is the surface efficiency for destruction of the species, \bar{c} the average velocity of the species and d the vessel diameter. a is a coefficient expressing the variation of diffusion coefficient with mixture composition, and is given^{7,8} by eqn (xiv)

$$a = [x_{\rm A} + (D_0^{\rm A}/D_0^{\rm B})x_{\rm B} + (D_0^{\rm A}/D_0^{\rm C})x_{\rm c}]^{-1}$$
(xiv)

where x_A , x_B and x_C are the mole fractions of the components.

The value of $R_3 = k_3/k_7^{\frac{1}{2}}$ has been obtained experimentally from a study⁸ of the oxidation of HCHO in KCl-coated vessels, where the HO₂ concentration is given by eqn (x), but with $2k_{11}$ [HCHO][O₂] replacing $2k_1$ [TMB]:

$$\mathrm{HCHO} + \mathrm{O}_2 \to \mathrm{HCO} + \mathrm{HO}_2. \tag{11}$$

 k_{11} was obtained by studies at very low HCHO concentrations, where the chain length is effectively zero. Since k_8 is known,^{5, 6} the unknown parameters determining the rate of HCHO oxidation are R_3 , k_6 and $k_{12}/k_7^{\frac{1}{2}}$

$$HO_{2} + HCHO \rightarrow H_{2}O_{2} + HCO.$$
 (12)

 $A_6[=A_0 \text{ in eqn (xiii)}]$ has been calculated⁹ for H_2O_2 using the method given by Hirschfelder et al.;¹⁰ use of $\sigma(N_2) = 0.375$ nm, $\sigma(H_2O_2) = 0.40$ nm and $\sigma(O_2) = 0.354$ nm gives $A_6 = 850$ Torr s⁻¹ at 500 °C for N₂ in a 5.1 cm diameter vessel, and $a(O_2) = 0.989$ relative to $a(N_2) = 1$. Use of $\sigma(TMB) = 0.745$ nm gives a(TMB) = 3.23. The value of A_6 varies with temperature, but the values of a are effectively constant. A value of $k_{12}/k_7^{\frac{1}{2}}$ has been obtained¹¹ by studying the effect of HCHO on the induction period of the $H_2 + O_2$ reaction at 500 °C in 5.1 cm diameter aged boric-acid-coated vessels. The only unknowns are thus R_3 and B_6 , which relates k_6 to A_6 via eqn (xiii). Optimisation of the agreement between the observed and calculated value of the CO yield at various times for various mixtures at 500 °C gave $R_3 = 4.56 \text{ (Torr}^3 \text{ s}^{-1})^{\frac{1}{2}}$ and $B_6 = 255 \text{ Torr} (M = N_2)$. The value of R_3 is very close to the value of 4.28 calculated from A_3 on the assumption that the diffusion constants for HO₂ are the same as those for H_2O_2 . The difference of ca. 7% could be due to small errors in any of the quantities $k_{12}/k_7^{\frac{1}{2}}$ obtained from the H₂+O₂ induction periods in the presence of HCHO, with an estimated error of $\pm 10\%$, R_a obtained from the HCHO+O₂ system with an estimated error of $\pm 10\%$, the diffusion coefficient or the value (2.0×10^9) taken for k_7 . Consequently, the experimental value of $R_3 = 4.56$ $(\text{Torr}^3 \text{ s}^{-1})^{\frac{1}{2}}$ at 500 °C has been taken, together with the calculated value of A_6 for H₂O₂. Values at other temperatures have been calculated from the change in diffusion coefficient with temperature given by the treatment of Hirschfelder et al.¹⁰

The optimum value of B_6 [for H_2O_2 in eqn (xiii)], and to a much lesser extent the value of R_3 , differ from those quoted earlier⁸ of 161 and 4.64, respectively. This is because the earlier results of HCHO+O₂ have been treated to allow for the interaction⁷ between the uniform profile of chain centres throughout the vessel,

R. R. BALDWIN, M. W. M. HISHAM, A. KEEN AND R. W. WALKER 1169

resulting from homogeneous termination processes, and the diffusion profile created by an efficient surface termination. In the case of a homogeneous initiation process, θ , such as the decomposition of TMB, which is uniform throughout the vessel, this interaction has been studied⁷ by solving the differential eqn (xv) by numerical integration methods:

$$D\frac{\mathrm{d}_2 n}{\mathrm{d}x^2} + (D/x)\frac{\mathrm{d}n}{\mathrm{d}x} - \delta n^2 + \theta = 0. \tag{xv}$$

n is the chain-centre concentration, *x* the vessel coordinate, δ the mutual homogeneous destruction constant and θ the initiation rate. Both with linear (first-order) homogeneous termination, where algebraic solution is possible,^{7, 12} and with mutual (second-order) termination, the interaction may reduce the radical concentration by up to 20% below the value calculated assuming no interaction. Both in the HCHO + O₂ system and in the TMB + O₂ system, the interaction is further complicated by the fact that the dissociation of H₂O₂ is a secondary source of initiation; since H₂O₂ is formed, by reactions (4) and (7), from HO₂ which is not at a uniform concentration throughout the vessel, and since H₂O₂ is predominantly destroyed at the surface [although by a process that is only moderately efficient at most pressures if $B_6 = 255$ Torr (M = N₂)], the total initiation process is not uniform. This difficulty was overcome by solving the two stationary-state simultaneous differential eqn (xvi) and (xvii)

$$D_n \frac{\mathrm{d}^2 n}{\mathrm{d}t^2} + (D_n/x) \frac{\mathrm{d}n}{\mathrm{d}x} - \delta n^2 + 2k_1 [\mathrm{TMB}] + 2k_8 [\mathrm{M}] p = 0 \qquad (\mathrm{xvi})$$

$$D_{p}\frac{d^{2}p}{dt^{2}} + (D_{p}/x)\frac{dp}{dx} - k_{8}[M]p + 0.5 \ \delta n^{2} + k_{4}n[TMB] = 0 \qquad (xvii)$$

where $n = [HO_2]$, $p = [H_2O_2]$, and D_n , D_p are the corresponding diffusion coefficients. These equations were solved numerically by the method used to solve⁷ the single eqn (xv). With eqn (xv), it is necessary to guess n_0 , the value of n at the centre of the vessel, to start the integration procedure, and the program varies this starting value until satisfactory convergence of successive solutions has been achieved. With a high ratio of homogeneous to surface termination, the initial value of n_0 has to be located with increasing accuracy, otherwise unreal solutions are obtained. With eqn (xvi) and (xvii), initial values of both n_0 and p_0 have to be provided, and accurate estimates are required, particularly at high ratios of homogeneous termination to surface termination, so that several trials are often necessary. Since incorporation of this procedure into the main program, together with optimisation procedures, would make the running time excessively long, eqn (xvi) and (xvii) were solved separately, the volume average concentrations of HO₂ and H_2O_2 were compared with the concentrations obtained on the assumption of no interaction, and corrections obtained which could be inserted into the main program. Because of the presence of mutual termination it was also necessary to obtain corrections to the volume average of [HO₂]². The corrections to [HO₂] varied from 0 to -20%, to [HO₂]² from -25 to +25%, and to [H₂O₂] from -15 to +15%. However, although the accurate evaluation of the role of H₂O₂ is complex, interpretation is not particularly sensitive to the parameters used for the surface destruction of H_2O_2 since, under the conditions used to evaluate $HO_2 + TMB$, the contribution of the OH chain is reasonably small.

Results obtained in this way are summarised in table 2.

As table 1 shows, the contribution of the HO₂ chain is only some 20-30% even under the most favourable conditions. While the r.m.s. deviation between observed and calculated yields of IBE at 440 °C implies an accuracy of $ca. \pm 5\%$ in $k_4/k_7^{\frac{1}{2}}$, the

T/⁰C	no. of mixtures	range of [TMB]/Torr	$k_4/k_7^{rac{1}{2}}/(\mathrm{dm^3\ mol^{-1}\ s^{-1}})^{rac{1}{2}}$	r.m.s. dev. (%)	data
440	7	0.50-4.0	0.436	2.4	Evans ²
418	8	0.25-4.0	0.257	8.0	Keen13
437.5	9	0.25-4.0	0.455	2.8	Keen13
466	10	0.25-4.0	0.674	6.2	Keen ¹³

TABLE 2.—VALUES OF $k_4/k_2^{\frac{1}{2}}$ at various temperatures in KCl-coated vessels^a

^a In all cases the range of pressure was 60-500 Torr.

results are less satisfactory at 418 and 466 °C. Moreover, Nalbandyan¹⁴ has reported the detection of HO₂ radicals when H₂O₂ is decomposed on a KCl-coated surface. Such a possibility would increase the concentration of HO₂ radicals above the value calculated from the present mechanism, although it would be unimportant at low temperatures and pressures, since very little H₂O₂ is formed because HO₂ radicals predominantly undergo reaction (3). However, at higher temperatures and pressures reaction (7) becomes the dominant reaction, and formation of HO₂ radicals by surface decomposition of H₂O₂ might become important. No indication appears available from Nalbandyan's work of the yield of HO₂ radicals produced in this way.

BORIC-ACID-COATED VESSELS

In aged boric-acid-coated vessels, the surface is extremely inefficient⁶ both for the destruction of HO₂ and of H₂O₂. To avoid the difficult treatment of the interaction of homogeneous and heterogeneous termination, as well as the possible complication of surface decomposition of H₂O₂ to give HO₂ radicals, studies were made in aged boric-acid-coated vessels to see if results consistent with those in KCl-coated vessels could be obtained.

Fig. 1 shows the [IBE] against time curves at 440 °C in a 5.1 cm diameter aged boric-acid-coated vessel for a mixture containing 1 Torr of TMB, 3 Torr of O_2 and at various total pressures from 15 to 200 Torr, obtained by addition of N_2 . The curves are significantly autocatalytic and the extent of autocatalysis increases with pressure because of the M term in reaction (8). This contrasts with the effectively linear [IBE] against time curve over the first 5% of reaction in KCl-coated vessels, where the very low quasi-stationary concentration of H_2O_2 is reached in a time that is usually small compared with the earliest sampling time, so that the initial autocatalysis is not detected. In aged boric-acid-coated vessels, the autocatalysis persists far into the reaction, well beyond the 5% consumption of TMB that was normally set as a limit to avoid secondary reactions of IBE.

In boric-acid-coated vessels, as shown in table 3, the chain due to HO₂ radicals is significantly greater than in KCl-coated vessels at lower temperatures, although at higher temperatures the main termination process is reaction (7) with both types of surface. However, as table 3 also shows, the chain length due to OH is also greater because of the much higher yields of H₂O₂. Since the H₂O₂ increased continuously with time in the early stages, values corresponding to *ca*. 2% reaction are given in table 3. Operation at low pressure, by reducing the value of M in reaction (8), reduces the OH chain. A pressure of 15 Torr of O₂ + TMB was thus used, except at the lowest



FIG. 1.—Effect of inert gas addition on [IBE] against time relationship. 1 Torr TMB, 3 Torr O_2 , $+N_2$, 440 °C. \bigcirc , $N_2 = 11$ Torr; \times , $N_2 = 26$ Torr; \bigcirc , $N_2 = 56$ Torr; \bigcirc , $N_2 = 146$ Torr; \bigtriangledown , $N_2 = 196$ Torr.

TABLE 3.—VARIATION	OF	CHAIN	LENGTH	WITH	PRESSURE	AND	TEMPERATURE	IN	BORIC-ACID-
			CO.	ATED V	/ESSELS				

For each condition, sample time selected corresponds to ca. 2% reaction. TMB = 2 Torr.

		<u> </u>	chain rea	ction (%)		
	<u> </u>	HO ₂ chain			OH chain	<u></u>
<i>T/</i> °C	at 15 Torr	at 60 Torr	at 500 Torr	at 15 Torr	at 60 Torr	at 500 Torr
400	45	37	25	18	35	61
440	35	32	18	8	19	62
470	21	19	11	8	18	61
500	15	14	10	6	13	51

temperature of 400 °C, when the partial pressure of O₂ was 30 Torr and the total pressure was made up to 60 Torr by N₂ addition.

An algebraic method of allowing for the OH chain can be devised since, in boric-acid-coated vessels, k_3 and k_6 are zero, and in the absence of an HO₂ chain, the combination of eqn (v) and (x) simplifies to eqn (xviii)

$$\frac{\mathbf{d}[\mathbf{H}_2\mathbf{O}_2]}{\mathbf{d}t} = k_1[\mathbf{TMB}]. \tag{xviii}$$

For small consumption, this can be integrated to give eqn (xix)

$$[\mathbf{H}_2\mathbf{O}_2] = k_1[\mathbf{TMB}] t. \tag{xix}$$

With the same assumption, and neglecting the 1% contribution from reaction (10), substitution of this expression for $[H_2O_2]$ in eqn (xii) and eliminating [OH] between eqn (iv) and (xii) gives eqn (xx):



 $-d[TMB]/dt = k_1[TMB] + 2k_8[M]k_1[TMB]t.$ (xx)

FIG. 2.—Variation of k_{obs} with time in aged boric-acid-coated vessels. 440 °C, $k_{obs} = [IBE]/2[TMB]_0 t$. \bigcirc , $[TMB]_0 = 4$, $[O_2] = 11$ Torr; \triangle , $[TMB]_0 = 2$, $[O_2] = 13$ Torr; \square , $[TMB]_0 = 1$, $[O_2] = 14$ Torr; \bigtriangledown , $[TMB]_0 = 0.5[O_2] = 14.5$ Torr; \times , $[TMB]_0 = 0.25$, $[O_2] = 14.75$ Torr; \diamond , $[TMB]_0 = 0.1$, $[O_2] = 14.9$ Torr.

Integration of eqn (xx) for small consumptions gives eqn (xxi):

$$\Delta[IBE]/t = 2k_1[TMB] + 2k_1k_8[TMB][M]t.$$
(xxi)

Defining

$$k_{obs} = \Delta[IBE]/2[TMB] t$$

$$k_{obs} = k_1 + k_1 k_8[M] t.$$

The intercept of the plot $k_{obs} = \Delta [IBE]/2[TMB] t$ against t should thus give $k_{obs}^{\circ} = k_1$, the value when the OH chain is eliminated.

Fig. 2 shows that the plots of k_{obs} against *t* are linear. However, the intercept varies systematically with [TMB]. This arises because of the residual HO₂ chain, so that the rate equation is given, not by the simple expression (i), but by expression (iii). Thus, k_{obs}^{o} is given by eqn (xxii):

$$k_{obs}^{o} = k_1 + k_4 (k_1/k_2)^{\frac{1}{2}} [TMB]^{\frac{1}{2}}.$$
 (xxii)

A plot of the extrapolated values of k_{obs}° from fig. 2 plotted against $[TMB]^{\frac{1}{2}}$ gives a reasonably linear relationship, from which $k_1 = 2.7 \times 10^{-5} \text{ s}^{-1}$, $k_4/k_7^{\frac{1}{2}} = 0.52$ (dm³ mol⁻¹ s⁻¹)^{$\frac{1}{2}$} at 440 °C (fig. 3).

However, the extrapolation of the k_{obs} against t plot is sensitive to experimental error in measuring the small yields of IBE in the early stages of reaction, since at other temperatures the lines through the k_{obs} against t points do not always show the expected increase in gradient with increasing [TMB]. Greater accuracy in the value of k_1 and particularly of k_4/k_7^2 can be obtained by using a computer treatment which, in effect, puts a mean line of the correct gradient for the particular mixture through each set of (k_{obs}, t) points. Numerical integration of the differential eqn (iv)-(ix) is

FIG. 3.—Plot of k_{obs}^{o} against [TMB][‡]. 440 °C, data from intercepts of fig. 2.

carried out as for KCl-coated vessels, except that a differential equation is always written for H_2O_2 . Six TMB+ O_2 mixtures were chosen, with concentrations ranging from 0.1 to 4.0 Torr at a total pressure of 15 Torr, except at the lowest temperature of 400 °C where 30 Torr of O_2 was used with the total pressure adjusted to 60 Torr with N₂. For each mixture, the yield of IBE was measured at four times where the consumption of TMB was < 5%; under these conditions secondary reactions of IBE are negligible. As with KCl-coated vessels, an optimisation procedure adjusted values of the parameters k_1 and $k_4/k_7^{\frac{1}{2}}$ so as to give minimum r.m.s. deviation between observed and calculated IBE yields.

The only significant parameters determining the calculated [IBE] against t curve are $k_1, k_4/k_7^{\frac{1}{2}}$ and the parameters for decomposition of H_2O_2 . k_8 is accurately known, with $M = H_2$, but the value of M_8 , given by eqn (xxiii), depends on the value taken for TMB relative to H_2 in reaction (8). Because of the low pressure of O_2 and N_2 , TMB can make major contributions to M_8 [the value of M in reaction (8)]:

$$M_8 = 0.35[O_2] + 0.43[N_2] + a(TMB)[TMB].$$
(xxiii)

At each temperature, optimum values of k_1 and $k_4/k_7^{\frac{1}{2}}$ were obtained for values of a(TMB) = 1, 2.5, 5.0 and 10 relative to $H_2 = 1$. (The values of 0.35 and 0.43 for O_2 and N_2 have been obtained in previous studies.⁵) Unfortunately, the minimum r.m.s.



FIG. 4.—Plot of log $k_4/k_2^{\frac{1}{4}}$ against 1/*T*. Aged B_2O_2 -coated vessels: \times , a(TMB) = 1; \bigcirc , a(TMB) = 2.5; \bigcirc , a(TMB) = 5; \triangle , a(TMB) = 10. KCl-coated vessels: \bigoplus , a(TMB) = 2.5.

deviation for each value of a(TMB) did not vary sufficiently to enable the optimum value of a(TMB) to be determined. However, increasing a(TMB) had relatively little effect on k_1 , whereas the value of $k_4/k_7^{\frac{1}{2}}$ decreased significantly, as shown in fig. 4. Fig. 4 also gives the values obtained for $k_4/k_7^{\frac{1}{2}}$ over the range 418-466 °C in KCl-coated vessels. In KCl-coated vessels, where a value of a(TMB) = 2.5 was used, the value for $k_4/k_7^{\frac{1}{2}}$ is fairly insensitive to a(TMB), partly because the contribution from H_2O_2 dissociation is smaller, and partly because higher pressures of O_2 and N_2 were used, so that the contribution of TMB to M_8 is less important; variation of a(TMB) from 1 to 5 had negligible effect on k_1 , and only altered $k_4/k_7^{\frac{1}{2}}$ by 1%. Fig. 4 shows that inconsistent variation of $k_4/k_7^{\frac{1}{2}}$ with temperature is obtained when a(TMB) is given the unlikely high value of 10, and that a value of 2.5 gives the best consistency with the results in KCl-coated vessels. The best line through all the results, both in B_2O_3 - and KCl-coated vessels, gives $A_4/A_7^{\frac{1}{2}} = 4.4 \times 10^5 \text{ (dm}^3 \text{ mol}^{-1} \text{ s}^{-1})^{\frac{1}{2}}$, $E_4 - \frac{1}{2}E_7 = 81.7 \pm 8 \text{ kJ mol}^{-1}$. If the present value¹⁵ of $k_7 = 2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, independent of temperature, is accepted, $A_4 = 1.97 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $E_4 = 81.7 \pm 8 \text{ kJ mol}^{-1}$.

The value obtained for k_1 is insensitive to a(TMB), the variation being an increase of 20% at 400 °C and an increase of 4% at 520 °C as a(TMB) is increased from 1 to 10. The results, together with the r.m.s. deviation and the corresponding values of k_1 obtained in KCl-coated vessels, are summarised in table 4.

	aged B ₂ O ₃ -	aged B_2O_3 -coated vessel			
		r m s dev	KCl-coated vessel		
T∕°C	k_{1}/s^{-1}	(%)	k_{1}/s^{-1}		
400	1.45 × 10 ⁻⁶	15.8			
420	6.17 × 10 ⁻⁶	5.7			
440	2.77×10^{-5}	3.6	2.56×10^{-5a}		
470	1.70×10^{-4}	3.5	2.01×10^{-4a}		
500	1.37×10^{-3}	3.7	1.33×10^{-3a}		
520	4.05×10^{-3}	3.8	3.98×10^{-3a}		
542		_	1.29×10^{-2a}		

TABLE 4.—VALUES OF k_1 IN B_2O_3 - AND KCl-COATED VESSELS

 a These values differ slightly from those quoted in ref. (2) because of allowance for the interaction between homogeneous and heterogeneous termination.

The high r.m.s. deviation at 400 °C reflects the very small amount of reaction at the lowest TMB concentrations even with reaction times of 2000 s. Measurements at 400 and 420 °C were included to examine the possible effect of an inefficient surface destruction of H_2O_2 . However, both at 400 and 420 °C, introduction of values of k_6 in the range 0.001-0.008 s⁻¹ increased rather than reduced the values of the r.m.s. deviation. The values obtained for k_1 only changed by ca. 2% over the range $k_6 = 0-0.008 \text{ s}^{-1}$, whereas $k_4/k_7^{\frac{1}{2}}$ changed by ca. 15%. Little error is thus likely in the values of k_1 and $k_4/k_7^{\frac{1}{2}}$ due to surface destruction of H_2O_2 .

The best straight line through the values of k_1 in B_2O_3 -coated vessels (omitting the value at 470 °C) gives $A_1 = 1.26 \times 10^{17} \text{ s}^{-1}$, $E_1 = 295.8 \text{ kJ mol}^{-1}$. Combination of the results for the B_2O_3 - and KCl-coated vessels in table 4 gives $A_1 = 1.04 \times 10^{17} \text{ s}^{-1}$, $E_1 = 294.7 \text{ kJ mol}^{-1}$. These values may be compared with $A_1 = 1.08 \times 10^{17} \text{ s}^{-1}$, $E_1 = 295.1 \text{ kJ mol}^{-1}$ obtained from the studies in a KCl-coated vessel. The differences are within experimental error.

Examination of the scatter of the [IBE] against time data and the log k_1 against 1/T data suggests that individual values of k_1 are accurate to within $\pm 4\%$. A 4% error in k_1 at the extremes of the temperature range would give an error of 1% in E_1 . The estimated accuracy of E_1 is thus within ± 3 kJ mol⁻¹, consistent with the statistical accuracy of ca. 1%. The very close agreement with previously published values² ($A_1 = 1.20 \times 10^{17}$ s⁻¹, $E_1 = 295.4$ kJ mol⁻¹) confirms the validity of the suggested thermodynamic data^{2,16} for the t-butyl radical.

It has been suggested¹⁴ that the decomposition of H₂O₂ on a KCl-coated surface

may produce HO₂ radicals, although the fraction of H₂O₂ giving HO₂ radicals is not stated. The agreement of the values of k_1 with the two vessel coatings indicates that the previously published value of E_1 , from which the enthalpy and entropy of the t-C₄H₉ radical have been calculated, has not been distorted by such production. Moreover, the agreement of the two sets of values of $k_4/k_7^{\frac{1}{2}}$ suggests that in the range 420-470 °C such production of HO₂ radicals does not significantly increase the concentration of HO₂ in KCl-coated vessels.

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(PAPER 1/799)