# The Equilibrium between Tertiary Alkylperoxy-radicals and Tetroxide Molecules

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*Summary* Di-tertiary-alkyl tetroxide molecules are stable at low temperatures (below −115°) and are in equilibrium with the corresponding peroxy-radicals.

THE autoxidation of liquid hydrocarbons proceeds by a chain mechanism[1] in which the termination step is generally

$$RO_2\cdot + RO_2\cdot \rightarrow \text{non-radical products} \qquad (1)$$

where $RO_2\cdot$ represents a peroxy-radical. Kinetic, isotopic, and product studies[2] of autoxidation indicate that this reaction proceeds through a tetroxide intermediate ($RO_4R$) which may be merely an activated complex or a molecule with an appreciable lifetime. Recent work has shown that di-t-butyl tetroxide can be prepared[3] below −80° and that in methylene chloride it is in equilibrium[4] with t-butylperoxy-radicals at temperatures in the range −110° to −85°.

During studies of the formation and decay of a variety of tertiary-alkylperoxy-radicals in hydrocarbon solvents we have found evidence for the existence of tetroxide molecules which are in equilibrium with the peroxy-radicals. Peroxy-radicals were produced by the photo-decomposition at −80° to −50° of di-t-butyl peroxide dissolved in an oxygen-saturated alkane [reactions (2)—(4)]. The concentration of peroxy-radicals was measured by e.s.r. (In each case the e.s.r. spectrum was a single line with a *g*-factor close to 2·015.) The attack of t-butoxy-radicals on the hydrocarbon [reaction (3)] is selective and as a result tertiary peroxy-radicals are formed more readily than primary or secondary peroxy-radicals. Also, tertiary peroxy-radicals terminate at a slower rate than the other peroxy-radicals[5] so that shortly after the end of photolysis only tertiary radicals remain. Following photolysis at −80° to −50° the samples were cooled to temperatures below −115°.

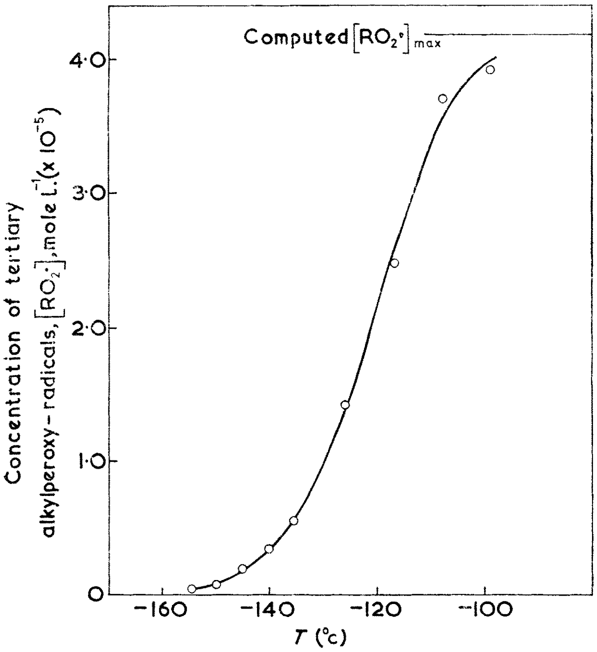

FIGURE. *Variation of* $[RO_2\cdot]$ *with temperature in* 2-*methylpentane. Circles indicate experimental points; the line indicates the computed curve.*

$$Me_3COOCMe_3 \xrightarrow{h\nu} 2Me_3CO\cdot \qquad (2)$$

$$Me_3CO\cdot + RH \longrightarrow Me_3COH + R\cdot \qquad (3)$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot \qquad (4)$$

Below −115° the irreversible decay of tertiary peroxy-radicals observed at higher temperatures is negligible. However, a further reduction in temperature causes the radical concentration to decrease rapidly to a new value which, once attained, shows no variation with time. The process is completely reversible within the temperature range −160° to −115°. The variation of concentration with temperature for tertiary peroxy-radicals derived from 2-methylpentane is shown in the Figure and similar results were obtained for tertiary peroxy-radicals derived from 2-methylbutane, 3-methylpentane, 2,3-dimethylbutane, 2,2,3-trimethylbutane, and cumene.

Our results show that there is a temperature-dependent equilibrium between peroxy-radicals and a non-radical product or products. An equilibrium that involves the combination of t-butoxy-radicals and peroxy-radicals cannot account for the results, as t-butoxy-radicals produced by photolysis at −115° are rapidly converted into peroxy-radicals [reactions (2)—(4)]. The observed dependence of the radical concentration on temperature is attributed therefore to an equilibrium between two peroxy-radicals and a tetroxide molecule, a process which involves the formation or scission of only one bond.

$$2RO_2\cdot \rightleftharpoons RO_4R \qquad (5)$$

$$K = [RO_4R]/[RO_2\cdot]^2 \qquad (6)$$

The variation of the equilibrium constant ($K$) with temperature ($T$) can be described by an integrated form of the van't Hoff isochore,

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (7)$$

where $\Delta S^\circ$ and $\Delta H^\circ$ are the changes in entropy and enthalpy.

Equations (6) and (7) are combined to give

$$\ln[RO_4R] - 2\ln[RO_2\cdot] = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (8)$$

As no irreversible decay occurs at temperatures below −115° the concentrations of tetroxide molecules and peroxy-radicals are related by

$$2[RO_4R] + [RO_2\cdot] = [RO_2\cdot]_{max} \qquad (9)$$

where $[RO_2\cdot]_{max}$ is the radical concentration at complete dissociation.

Combination of equations (8) and (9) gives

$$\ln([RO_2\cdot]_{max} - [RO_2\cdot]) - 2\ln[RO_2\cdot] - \ln 2 = \frac{\Delta S^0}{\boldsymbol{R}} - \frac{\Delta H^0}{\boldsymbol{R}T} \qquad (10)$$

The value of $[RO_2\cdot]_{max}$ cannot be determined experimentally, since at temperatures where dissociation of the tetroxide is nearly complete the irreversible decay of the peroxy-radicals is appreciable. Thus, the values of $[RO_2\cdot]_{max}$, $\Delta H^0$ and $\Delta S^0$ which give the best agreement between the experimental and predicted results for the variation of $[RO_2\cdot]$ with temperature (Figure) were calculated by a curve-fitting process using a computer. The values of $\Delta H^0$ and $\Delta S^0$ which are listed in the Table are in excellent agreement with those obtained independently by Adamic, Howard, and Ingold (see ref. 6).

Although these values of $\Delta H^0$, together with that for t-butylperoxy-radicals[4] (−6 kcal. mole$^{-1}$), lie within the range of values calculated by Benson[7] using group additivity relationships they are above his mean value. Further, the fact that a reversible equilibrium involving peroxy-radicals is observed in the temperature range −160° to −115° shows that tetroxides are stable at higher temperatures than that of −170° estimated by Benson.[7]

If the self-termination reaction of peroxy-radicals proceeds through a tetroxide intermediate [reaction (11)] then the experimentally determined

$$RO_2\cdot + RO_2\cdot \overset{K}{\rightleftharpoons} RO_4R \xrightarrow{k_1} \text{non-radical products} \qquad (11)$$

termination rate constant, $k$ is equivalent to $Kk_1$. It has been found[8] that, for 2,2,3-trimethylbutane, $k = 10^{9\cdot2 \pm 1\cdot0} \exp[(7\cdot5 \pm 1\cdot0)/\boldsymbol{R}T]$ mole$^{-1}$ l.sec.$^{-1}$. Combination of this result with the values of $\Delta S^0$ and $\Delta H^0$ given in the Table

*Values of* $\Delta H^0$ *and* $\Delta S^0$ *for the equilibrium* $2RO_2\cdot \rightleftharpoons RO_4R$

| Parent hydrocarbon | $\Delta H^0$ kcal. mole$^{-1}$ | $\Delta S^0$ cal. deg.$^{-1}$ mole$^{-1}$ |
|---|---|---|
| 2-Methylbutane .. | $-8\cdot9 \pm 1\cdot0$ | $-36 \pm 8$ |
| 2-Methylpentane .. | $-8\cdot9 \pm 0\cdot7$ | $-39 \pm 6$ |
| 3-Methylpentane .. | $-9\cdot7 \pm 0\cdot5$ | $-44 \pm 4$ |
| 2,3-Dimethylbutane .. | $-8\cdot2 \pm 0\cdot5$ | $-34 \pm 4$ |
| 2,2,3-Trimethylbutane | $-8\cdot7 \pm 1\cdot0$ | $-38 \pm 7$ |
| Cumene .. .. | $-11\cdot2 \pm 0\cdot9$ | $-48 \pm 7$ |

gives the following Arrhenius parameters for the irreversible decay of the tetroxide molecule; $A_1 = 10^{17\cdot5 \pm 2\cdot4}$ sec.$^{-1}$, $E_1 = 16\cdot2 \pm 2\cdot0$ kcal. mole$^{-1}$.

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