*The Reactions of Methyl Radicals with Acetone, Diethyl Ketone, and Di-*tert.*-butyl Peroxide.*

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The thermal decomposition of di-*tert.*-butyl peroxide between 130° and 155° has been reinvestigated and the rate constant for the initial fission of the O–O bond found to be $4 \times 10^{16}e^{-39,000/RT}$ sec.$^{-1}$.

The rate constants for the hydrogen abstraction reactions of thermal methyl radicals with di-*tert.*-butyl peroxide, acetone, and diethyl ketone are given by $25 \times 10^{11}e^{-11,700/RT}$, $6{\cdot}4 \times 10^{11}e^{-9500/RT}$, and $6{\cdot}4 \times 10^{11}e^{-8000/RT}$ mole^{-1} c.c. sec.$^{-1}$, respectively.

RALEY, RUST, and VAUGHAN (*J. Amer. Chem. Soc.*, 1948, **70**, 88) have shown that the thermal decomposition of di-*tert.*-butyl peroxide is an essentially non-chain unimolecular process, leading predominantly to the formation of acetone and ethane by the following mechanism :

$$CMe_3{\cdot}O{\cdot}O{\cdot}CMe_3 \xrightarrow{k_1} 2CMe_3{\cdot}O{\cdot} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$CMe_3{\cdot}O{\cdot} \xrightarrow{k_2} COMe_2 + CH_3{\cdot} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$CH_3{\cdot} + CH_3{\cdot} \xrightarrow{k_3} C_2H_6 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

A small amount of methane was formed, probably by the reactions

$$CH_3{\cdot} + CMe_3{\cdot}O{\cdot}O{\cdot}CMe_3 \longrightarrow CH_4 + CMe_3{\cdot}O{\cdot}O{\cdot}CMe_2{\cdot}CH_2{\cdot} \quad . \; . \; . \quad (4)$$

$$CMe_3{\cdot}O{\cdot}O{\cdot}CMe_2{\cdot}CH_2{\cdot} + CH_3{\cdot} \longrightarrow CMe_3{\cdot}O{\cdot}O{\cdot}CMe_2{\cdot}CH_2Me \quad . \; . \; . \; . \; . \quad (5)$$

In the gas phase, in the presence of various organic substrates RH, the *tert.*-butoxy-radical is presumed to exhibit no other reactions than (2), which is very fast, but additional reactions of the type (6) can occur.

$$CH_3{\cdot} + RH \xrightarrow{k_6} R{\cdot} + CH_4 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

The purpose of this investigation was to use thermal methyl radicals to study reaction (6) for substances (RH) which are photolytic sources of higher radicals, and whose absorption spectra are such that they themselves would be photolysed if the usual photolytic sources of methyl radicals, dimethylmercury and acetone, were used.

Incidentally, the thermal decomposition of the peroxide was again studied, the rate being measured by the formation of ethane and methane, since the decomposition of each molecule of peroxide leads to the formation of either one molecule of ethane or one of methane.

If RH is acetone, (6) becomes

$$CH_3{\cdot}CO{\cdot}CH_3 + CH_3{\cdot} \longrightarrow CH_3{\cdot}CO{\cdot}CH_2{\cdot} + CH_4 \quad . \; . \; . \; . \; . \; . \quad (7)$$

The acetonyl radical then reacts with a methyl radical

$$CH_3\cdot CO\cdot CH_2\cdot + CH_3\cdot \longrightarrow CH_3\cdot CO\cdot C_2H_5 \qquad . \; . \; . \; . \; . \; . \quad (8)$$

to form ethyl methyl ketone. This compound was isolated by Raley, Rust, and Vaughan (*loc. cit.*) from the reaction products of the complete decomposition of the peroxide and was presumably formed by the products of (2) reacting together according to (7) and (8). Consequently, to evaluate correctly the methane formed in (6), the methane formed from the products of (2) must be effectively suppressed. For this reason a high RH concentration is used, and only a small percentage of the peroxide is decomposed. The latter requirement is most important in the investigation of (4), because RH is now di-*tert*.-butyl peroxide itself, and increase of its concentration only serves to increase the rate of (1) and thus the rate of (2) by a proportionate amount.

From the above reaction scheme the rate of methane formation is given by

$$d[CH_4]/dt = R_{CH_4} = k_6[CH_3\cdot][RH]$$

and of ethane by

$$d[C_2H_6]/dt = R_{C_2H_6} = k_3[CH_3\cdot]^2$$

whence

$$k_6/k_3^{\frac{1}{2}} = R_{CH_4}/R^{\frac{1}{2}}_{C_2H_6}[RH]$$

The plot of log $k_6/k_3^{\frac{1}{2}}$ against $1/T$ gives $E_6 - \frac{1}{2}E_3$ and $A_6/A_3^{\frac{1}{2}}$, where T is the absolute temperature, E is the activation energy, and A is the frequency factor. By using Gomer and Kistiakowsky's values (*J. Chem. Physics*, 1951, **19**, 85) of $E_3 = 0$ kcal./mole and $A_3 = 4{\cdot}5 \times 10^{13}$ mole^{-1} c.c. sec.$^{-1}$ for the recombination of methyl radicals, E_6 and A_6 can be obtained.

Experimental.—The method was to mix measured pressures of the peroxide and ketone in a 2-l. volume surrounded by a steam jacket. This mixture was expanded into a 3-l. reaction vessel immersed in an oil-bath thermostat which could be controlled to ±0·1° for the period of an experiment. The reaction was terminated by pumping the reactants and products through wide-bore tubing and a liquid-nitrogen trap into a 3-l. bulb. The ethane was collected in liquid-nitrogen traps, and the methane was pumped from the collecting system by a mercury diffusion pump into an analysis system, which consisted of a Töpler pump and a gas burette. When the volume of methane had been measured, the ethane was pumped into the analysis system through traps kept at −160°, and its volume measured.

RESULTS AND DISCUSSION

In all the runs about 10% of the peroxide was decomposed. When RH was ketone, [RH] was taken as the initial concentration, which was always 1·5—3 times greater than the peroxide concentration. Not more than 0·5% of the acetone reacted, yielding 7—14% of methane of the total methane and ethane formed, and between 2 and 4% of the diethyl ketone reacted, the amount of methane formed varying between 31 and 55%.

TABLE 1.

System *	E_1, kcal./mole	A_1, sec.$^{-1}$	k_1, sec.$^{-1}$ (145°)	Source †
Peroxide	38·6	$1{\cdot}9 \times 10^{16}$	$1{\cdot}3 \times 10^{-4}$	This work
Peroxide–acetone	39·5	$5{\cdot}9 \times 10^{16}$	$1{\cdot}3 \times 10^{-4}$	,,
Peroxide–diethyl ketone	39·5	$6{\cdot}8 \times 10^{16}$	$1{\cdot}5 \times 10^{-4}$	,,
Peroxide	39·1	$3{\cdot}2 \times 10^{16}$	$1{\cdot}1 \times 10^{-4}$	*a*
Peroxide	36—40	6×10^{14}—6×10^{16}	1×10^{-4}	*b*
Peroxide–acetone	37	9×10^{14}	$0{\cdot}6 \times 10^{-4}$	*c*
Peroxide–toluene (flow system)	36 ± 1	4×10^{14}—7×10^{14}	$1{\cdot}3 \times 10^{-4}$	*d*
Peroxide–toluene (static system)	34 ± 2	4×10^{13}	$0{\cdot}6 \times 10^{-4}$	*d*
Peroxide	38	7×10^{15}	—	*e*

* Peroxide = di-*tert*.-butyl peroxide.

† *a*, Raley, Rust, and Vaughan, *loc. cit.*; *b*, Brinton and Volman, *J. Chem. Physics*, 1952, **20**, 25; *c*, Jaquiss, Roberts, and Szwarc, *J. Amer. Chem. Soc.*, 1952, **74**, 6005; *d*, Murawski, Roberts, and Szwarc, *J. Chem. Physics*, 1951, **19**, 698; *e*, Lossing and Tickner, *J. Chem. Physics*, 1952, **20**, 907 [this is a composite result of the high-temperature runs (280—350°) of these authors together with the results of *a* and *d*].

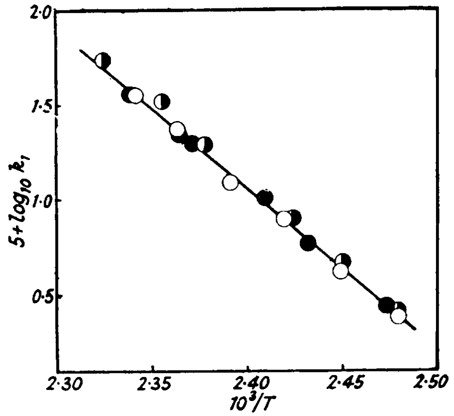
When RH was di-*tert*.-butyl peroxide, [RH] was taken as the arithmetic mean of the initial and final concentrations of the peroxide, the proportion of methane formed being between 2 and 3%.

The values of E_1, A_1, and k_1 at 145° which have been obtained from Fig. 1 are given in Table 1, together with experimental values of other workers. The present results are seen to lead to a value of E_1 of 39 ± 0·5 kcal./mole, with A_1 about 4×10^{16} sec.$^{-1}$.

In Table 2 the values of E_6, A_6, and k_6 at 182° obtained from Fig. 2 are given, together with the results of other workers.

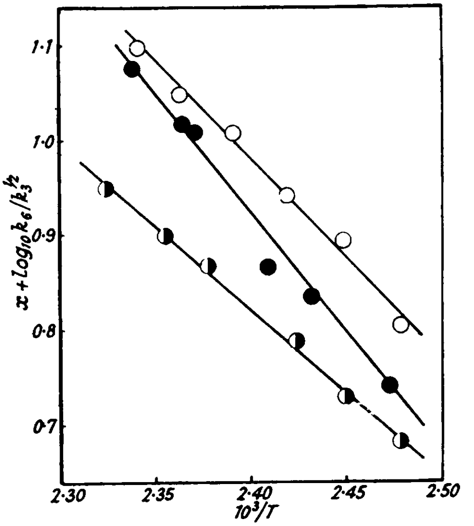
The activation energy obtained for the reaction of methyl radicals with acetone is in excellent agreement with the results of other workers, using both photolytic and thermal methyl radicals. There is a sensible decrease in the activation energy obtained for the reaction with diethyl ketone, in accordance with the general trend exhibited by compounds containing only primary hydrogen atoms, and those containing both primary and secondary hydrogen atoms.

FIG. 1.



Arrhenius plots for the thermal decomposition of di-*tert.*-butyl peroxide : ● alone, ○ in the presence of acetone, and ◑ in the presence of diethyl ketone.

FIG. 2.



Arrhenius plots for reaction of methyl radicals with : ○ Acetone, $x = 1$, ◑ diethyl ketone, $x = 0$, and ● di-*tert.*-butyl peroxide, $x = 1{\cdot}48$.

TABLE 2.

RH *	E_6, kcal./mole †	A_6, mole^{-1} c.c. sec.$^{-1}$	k_6, mole^{-1} c.c. sec.$^{-1}$ (182°)	Source ‡
Acetone	9·5 ± 0·3	$6{\cdot}4 \times 10^{11}$	$1{\cdot}6 \times 10^{7}$	This work
,, ...	9·7 ± 0·1	$4{\cdot}0 \times 10^{11}$	$1{\cdot}0 \times 10^{7}$	*a*
,, ...	9·6 ± 0·4	$3{\cdot}0 \times 10^{11}$	$0{\cdot}8 \times 10^{7}$	*b* §
,, ...	9·5 ± 0·2	$4{\cdot}0 \times 10^{11}$	$1{\cdot}1 \times 10^{7}$	*c*
,, ...	9·5 ± 1·0	$2{\cdot}7 \times 10^{11}$	$0{\cdot}9 \times 10^{7}$	*d*
Diethyl ketone	8·0 ± 0·2	$6{\cdot}4 \times 10^{11}$	$9{\cdot}1 \times 10^{7}$	This work
Peroxide	11·7 ± 0·3	25×10^{11}	$0{\cdot}6 \times 10^{7}$	,,
Peroxide	(15)	(300×10^{11})	$0{\cdot}2 \times 10^{7}$	*e* §

* Peroxide = di-*tert.*-butyl peroxide.

† The probable errors in the activation energies are derived solely from consideration of the deviations of the points from the Arrhenius relationship.

‡ *a*, Trotman-Dickenson and Steacie, *J. Chem. Physics*, 1950, **18**, 1097; *b*, Saunders and H. A. Taylor, *ibid.*, 1941, **9**, 616; *c*, Gomer and Kistiakowsky, *loc. cit.*; *d*, Jaquiss, Roberts, and Szwarc, *loc. cit.*; *e*, Brinton and Volman, *loc. cit.*

§ These quantities were not calculated in this manner by the original authors (see Trotman-Dickenson, *Quart. Reviews*. 1953, **7**, 198).

Kutschke, Wijnen, and Steacie (*J. Amer. Chem. Soc.*, 1952, **74**, 714), using diethyl ketone as a source of ethyl radicals, studied the reaction

$$C_2H_5\cdot + C_2H_5{\cdot}CO{\cdot}C_2H_5 \longrightarrow C_2H_6 + \text{etc.} \qquad \ldots\ldots \quad (9)$$

They found $E_9 = 7{\cdot}4$ kcal./mole, with a steric factor of about 3×10^{-4}. The greater energy of activation required for the methyl (8·0 kcal./mole) than the ethyl (7·4 kcal./mole) radical reaction is surprising, for one would expect that the ethyl radical reaction would require, if anything, a slightly higher activation energy than the methyl radical reaction, because the C–H bond strength in methane exceeds that in ethane by about 5 kcal./mole.

The activation energy for methyl radical attack on di-*tert.*-butyl peroxide is surprisingly high, only methane requiring a higher activation energy of approximately 12·8 kcal./mole (Trotman-Dickenson and Steacie, *J. Phys. Colloid Chem.*, 1951, **55**, 908), whilst other compounds containing only primary C–H bonds have lower activation energies than the 11·7 kcal./mole required for di-*tert.*-butyl peroxide; *e.g.*, ethane 10·4 and 2 : 2 : 3 : 3-tetramethylbutane 9·5 kcal./mole (Trotman-Dickenson, Birchard, and Steacie, *J. Chem. Physics*, 1951, **19**, 163). The reason why this should be is not clear.

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