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THE ARRHENIUS PARAMETERS FOR THE THERMAL DECOMPOSITION OF ORGANIC PEROXIDES, AND THE DISSOCIATION ENERGY OF THE PEROXIDE BOND

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Abstract—The literature data on the Arrhenius parameters for the thermal decomposition of dialkyl, alkyl aralkyl and diaralkyl peroxides are compared in an attempt to remove the discrepancies between the quoted values for the activation energy, E, which is generally identified with the dissociation energy of the peroxide bond, D(RO—OR′). The collected data not only confirm there to be differences between the values of E for different peroxides (the extreme values being 31·3 ± 1·0 kcal mole^{-1} for diethyl peroxide, and 37·8 ± 1·0 kcal mole^{-1} for di-t-butyl peroxide), but also show up a correlated variation in the pre-exponential factor, A (the corresponding extremes being about 10^{13} sec^{-1}, and about 10^{16} sec^{-1}), involving a linear ("isokinetic") relationship between log A and E, with an isokinetic temperature, T_1, of 210°, at which the rate constant, k_1, is 0·1 sec^{-1}. The possible explanations for these results are examined, but none of them either clarify the variations in the Arrhenius parameters or indicate what is the correct value for D(RO—OR′).

ORGANIC peroxides, and the alkoxy radicals produced through the scission of their peroxide (—O—O—) bonds, play an important role as intermediates in many types of organic reactions, especially such technically important ones as autoxidation and combustion; it is therefore necessary to have an accurate estimate of the strength, i.e. the dissociation energy, of the peroxide bond in order to completely understand both the thermochemistry of these compounds and the mechanism of their reactions. Since this bond is generally by far the weakest in the molecule of a particular peroxide, ROOR′, its dissociation energy, D(RO—OR′), is most conveniently determined by the direct kinetic method,[1] whereby D(RO—OR′) is equated to the activation energy, E, of the homolytic unimolecular scission

$$\mathrm{ROOR'} \rightarrow \mathrm{RO\cdot} + \mathrm{R'O\cdot} \tag{1}$$

as estimated from the Arrhenius equation

$$k = A \exp(-E/RT) \tag{2}$$

where k is the first-order rate constant for the thermal decomposition process involving the scission (1) as its rate-determining step.

It is not safe to apply this approach to either hydroperoxides or diacyl peroxides, for these are so susceptible to radical attack that chain-induced decomposition contributes appreciably to the rate of their thermal decomposition,[2] so that the simple scission (1) is not the rate-determining step. However, the dialkyl, alkyl aralkyl and diaralkyl peroxides are known[2] to be much less susceptible to such radical-attack, and their thermal decomposition is the gas phase and in non-polar media is normally first

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[1] T. L. Cottrell, *The Strengths of Chemical Bonds* 2nd ed., chap. 4. Butterworths, London (1958).
[2] C. Walling, *Free Radicals in Solution* chap. 10. John Wiley, New York (1957).

TABLE 1. ARRHENIUS PARAMETERS FOR THE FIRST-ORDER THERMAL DECOMPOSITION OF DIALKYL, ALKYL ARALKYL, AND DIARALKYL PEROXIDES, ROOR′; EXCEPT WHERE OTHERWISE STATED, THE REACTION WAS STUDIED ON THE PURE VAPOUR IN A STATIC SYSTEM.

Serial letter	Substituent groups		Temp range, °C	Reaction conditions	log A/ sec^{-1}	E/kcal. mole^{-1}	Ref.
	R	R′					
a	Me	Me	155–180	10–50 torr[1]	15·60	36·9	3
b	Me	Me	113–143	3–30 torr	15·08	34·8	4
c	Et	Et	140–185	2–300 torr	13·55[2]	31·9	5
d	Et	Et	160–240	1–40 torr	12·32	30·4	6
e	Et	Et	200–245	*ca.* 0·1 torr[3]	13·56	32·4	7
f	Et	Et	130–170	3–11 torr	12·68	30·4	8
g	Pr^n	Pr^n	146–176	0·2–3 torr	15·56[2]	35·9	9
h	Et	Bu^t	135–175	2–17 torr	14·40	34·5	8
i	Bu^t	Bu^t	140–160	50–390 torr	16·50	39·1	10
j	Bu^t	Bu^t	125–145	Solution in t-butylbenzene[4]	16·04	38·0	10
k	Bu^t	Bu^t	125–145	Solution in isopropylbenzene[4]	15·80	37·5	10
l	Bu^t	Bu^t	125–145	Solution in tributylamine[4]	15·54	37·0	10
m	Bu^t	Bu^t	116–167	10–40 torr[5]	12·69	32·2	11
n	Bu^t	Bu^t	178–272	0·04–17 torr[6]	15·20	36·5	11
o	Bu^t	Bu^t	280–350	*ca.* 2 mtorr[7]	15·21	36·0	12
p	Bu^t	Bu^t	130–155	—[8]	16·70	39·2	13
q	Bu^t	Bu^t	103–145	10–20 torr	16·40	38·7	14
r	Bu^t	Bu^t	130–160	27–130 torr	15·60	37·4	15
s	Bu^t	Bu^t	145–180	—[8]	16·14	38·1	16
t	Bu^t	$PhCMe_2$	128–158	Solution in dodecane[9]	14·36	34·3	17
u	$EtCMe_2$	$EtCMe_2$	132–150	40–360 torr	16·72[10]	38·7[10]	10
v	$PhCMe_2$	$PhCMe_2$	111–150	Solution in isopropylbenzene[11]	14·63	34·5	18

[1] The Arrhenius parameters were determined at 23 torr peroxide in presence of 400 torr MeOH; the reaction shown to be first order using stated pressure range in the absence of MeOH, the rate constant being the same as in its presence.

[2] Corrected for the factor of ln 10 omitted in the original papers.

[3] Flow system, with *ca.* 80-fold excess of toluene.

[4] Concentration: 1 molar.

[5] In the presence and in the absence of excess toluene.

[6] Flow system, in the presence of excess toluene or benzene.

[7] Flow system, with 6–12 torr He added; reaction followed by mass spectrometric estimation of methyl radical concentration. Arrhenius plot curved, concave upwards.

[8] Pressure range not stated.

[9] Concentration: 0·4 molar. Closely similar rates were obtained with isopropylbenzene and with t-butylbenzene as solvents.

[10] Rate constants extrapolated to zero pressure; of the four experimental points on the Arrhenius plot, the one at the lowest temperature lay well below the chosen line through the others.

[11] Concentrations: 0·04 and 0·18 molar. The points on the Arrhenius plot from the results of Kharasch *et al.* (Ref. 17) are too scattered for the plot to be useful.

order, giving products consistent with reaction (1) as the initial step; this suggests that with these types of peroxide the method ought to give a consistent value for E which is in turn identifiable with D(RO—OR′). Nevertheless, the two examples discussed most intensively by Cottrell,[1] diethyl peroxide and di-t-butyl peroxide, turn out to have E-values of 32 kcal mole^{-1} and 39 kcal mole^{-1} respectively; the difference between these two values is much greater than we would expect either between separate determinations of E or between the values of D(RO—OR′) for such a similar pair of compounds.

In an attempt to clear up this anomaly and decide what is the correct value of D(RO—OR′), an extensive survey has been made of the literature data[3–18] for the kinetics of the decomposition of dialkyl, alkyl aralkyl, and diaralkyl peroxides in the vapour phase, and in solution in non-polar media; the data are summarized in Table 1. With the exception of minor deviations noted in the table, all the decompositions were first order; the usual tests on the vapour-phase decompositions showed them to be homogeneous. The Arrhenius parameters quoted in the table have been checked using either the original rate constants or, where these were not available, the original Arrhenius plots; except for the single case noted in the table, all the Arrhenius plots were linear.

For convenience of discussion, a serial letter (a, b, c, etc.) has been allocated to each study of a particular peroxide by a particular worker or group of workers. As Table 1 shows, a few peroxides (diethyl peroxide and di-t-butyl peroxide particularly) have been studied by a number of groups of workers; however, the data from these studies on the same peroxide have been kept separate to give as consistent a picture as possible of the typical uncertainty to be expected in the Arrhenius parameters from a given study (thus, no attempt has been made to obtain a "best" pair of parameters from a combined Arrhenius plot); to this same end, the results of Szwarc and his co-workers[11] on di-t-butyl peroxide have been taken as two separate sets of data giving distinct pairs of Arrhenius parameters (serial letters m and n), since they were obtained by different experimental techniques (static, and flow) over distinct and separate ranges of temperature.

The comprehensive data in Table 1 show that the spread in the values of E is quite general for this type of compound, the range now extending from 30·4 kcal mole^{-1} (d and f) to 39·2 kcal mole^{-1} (p); these limits, however, still relate to diethyl peroxide

[3] Y. Takezaki and C. Takeuchi, *J. Chem. Phys.* **22**, 1527 (1954).
[4] P. L. Hanst and J. G. Calvert, *J. Phys. Chem.* **63**, 104 (1959).
[5] E. J. Harris and A. C. Egerton, *Proc. Roy. Soc.* (London) **168**, Series A, 1 (1938).
[6] K. Moriya, *Rev Phys. Chem. Japan, Shinkichi Horiba Commem. Vol.*, 143 (1946).
[7] R. E. Rebbert and K. J. Laidler, *J. Chem. Phys.* **20**, 574 (1952).
[8] J. R. Harrison, Ph.D. thesis, University of London (1952).
[9] E. J. Harris, *Proc. Roy. Soc.* (London) **173**, Series A, 126 (1939).
[10] J. H. Raley, F. F. Rust and W. E. Vaughan, *J. Amer. Chem. Soc.* **70**, 88 and 1336 (1948).
[11] J. Murawski, J. S. Roberts and M. Szwarc, *J. Chem. Phys.* **19**, 698 (1951).
[12] F. P. Lossing and A. W. Tickner, *J. Chem. Phys.* **20**, 907 (1952).
[13] G. O. Pritchard, H. O. Pritchard and A. F. Trotman-Dickenson, *J. Chem. Soc.* 1425 (1954).
[14] A. R. Blake and K. O. Kutschke, *Canad. J. Chem.* **37**, 1462 (1959).
[15] L. Batt and S. W. Benson, *J. Chem. Phys.* **36**, 895 (1962).
[16] J. Long and G. Skirrow, *Trans. Faraday Soc.* **58**, 1403 (1962).
[17] M. S. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem.* **16**, 105 (1951).
[18] H. C. Bailey and G. W. Godin, *Trans. Faraday Soc.* **52**, 68 (1956).

and di-t-butyl peroxide respectively. At the same time, the values of the pre-exponential factor, A, also show a wide spread, from $2{\cdot}1 \times 10^{12}$ sec^{-1} (d) to $5{\cdot}0 \times 10^{16}$ sec^{-1} (p), as contrasted with a value of close to 10^{13} sec^{-1} to be expected for a unimolecular reaction.[19] The values in the Table also show there to be a correlation between A and E. This is confirmed by Fig. 1, in which log A is plotted against E; the correlation between the plotted quantities is seen to be close to linear. The equation of the line best fitting the total of 22 points (continuous line in Fig. 1) is

$$\log A\ (\text{sec}^{-1}) = 0{\cdot}45E\ (\text{kcal mole}^{-1}) - 1.0 \qquad (3)$$

The broken lines in Fig. 1, which enclose two-thirds of the points and hence represent an estimate of the standard deviation, correspond either to an overall spread in log A

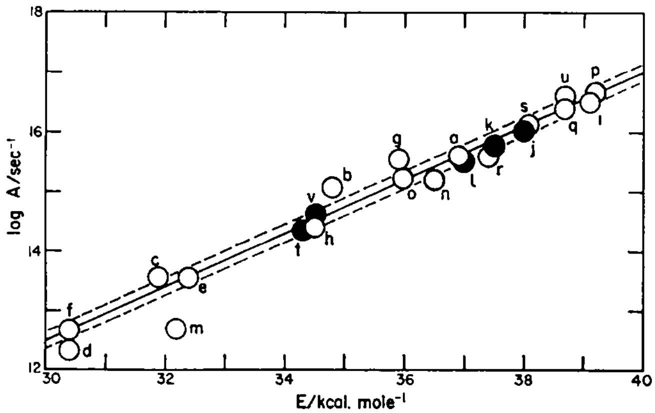

FIG. 1. Arrhenius parameters for the thermal decomposition of dialkyl, alkyl aralkyl, and diaralkyl peroxides in the vapour phase (open circles) and in solution (filled circles). The key to the lettering of the points is given in Table 1.

of 0·3 (i.e. a factor of 2 in A itself) or alternatively to a spread of 0·5 kcal mole^{-1} in E; these would seem to be more realistic estimates of the uncertainties in A and E than those estimated from the Arrhenius plots and indicated by the significant figures in the values in Table 1.

The present type of linear correlation between log A and E is usually termed an "isokinetic relationship", since it implies that there is a particular temperature (the "isokinetic temperature", T_i) at which the rate constants become identical. For the present case, Eq. (3) gives $T_i = 483$°K (210°C), at which $k_i = 0{\cdot}1$ sec^{-1}; in the few cases (d, e, n) where the actual experimental temperature range extended up to 210° the actual rate constants obtained are close to 0·1 sec^{-1}. Correlations of this type are encountered fairly frequently in the kinetics of organic reactions,[20] but in the majority of cases they correspond to either molecular or ionic reactions in solution; in fact there are no clear-cut examples comparable to the present type of homolytic scission. In addition, there is no coherent theory to explain isokinetic relationships in general, and formal approaches from the transition state theory in terms of a correlation between the enthalpy and entropy changes of activation[21] are of little use precisely

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[19] B. G. Gowenlock, *Quart. Revs* **14**, 133 (1960).

[20] J. E. Leffler, *J. Org. Chem.* **20**, 1202 (1955).

[21] J. E. Leffler and E. Grunwald, *Rates and Equilibria of Organic Reactions* chap. 9. John Wiley (1963).

because of the lack of such a theoretical background. For these reasons, in the present discussion the Arrhenius parameters will be treated largely on a phenomenological basis.

Since the correlation between E and $\log A$ is so close, it becomes convenient to consider only one of them, E, in discussing the order of their values for different peroxides. As Fig. 1 shows, the individual peroxides tend to occur in clusters along the correlation line; the spread in the values of E for the most intensively studied peroxides, diethyl peroxide (c through f) and di-t-butyl peroxide (i through s), suggests strongly that for a peroxide in general, the standard deviation in this parameter is about 1 kcal mole^{-1}, which is comparable to the interval between these clusters; nevertheless, one can still put the E-values for the clusters of the symmetrical peroxides ($R = R'$) fairly definitely (in terms of their substituent groups R) as:

$$\mathrm{Et} < \mathrm{PhCMe_2} < \mathrm{Me} \simeq \mathrm{Pr^n} < \mathrm{Bu^t} \simeq \mathrm{EtCMe_2} \tag{4}$$

while the values for the two unsymmetrical compounds which remain, ethyl t-butyl peroxide and t-butyl α-cumyl peroxide, lie very close to that for di-α-cumyl peroxide ($R = R' = \mathrm{PhCMe_2}$). It is curious that the mean value of E (34·4 ± 0·1 kcal mole^{-1}) for this cluster of three peroxides lies almost exactly halfway between that for diethyl peroxide (31·3 ± 1·0 kcal mole^{-1}) and that for di-t-butyl peroxide (37·8 ± 1·0 kcal mole^{-1}); in addition, the E-values for dimethyl and dipropyl peroxides can be taken to form a cluster centred at about 35·8 kcal mole^{-1}, which is again approximately halfway between the adjacent groups. This apparent "quantization" in the values of E (and, of course, of $\log A$) is more support for the validity of the series (4), and may also prove to have a theoretical significance, although no such significance emerges from the present discussion. Even the series (4), however, casts no real light on the reasons for the variations in the parameters or for the correlation between them, for the order of the R groups in the series (4) seems to have little connection with their size, structure or reactivity; thus dimethyl and dipropyl peroxides occur together at the upper end of the series while the compound of intermediate structure, diethyl peroxide, occurs right down at the lower end; again, although it seems reasonable that ethyl t-butyl peroxide should fall halfway in E-value between diethyl peroxide and di-t-butyl peroxide, nevertheless there seems no reason why di-α-cumyl peroxide and t-butyl α-cumyl peroxide should also fall in this same position. It is precisely this lack of connection between the structure of the substituent groups and the value of the Arrhenius parameters that makes the present variations in E and A, and the isokinetic relationship between them, so difficult to explain; the explanations that can be advanced for discussion are either over-generalized or else rather piecemeal; the most plausible can be discussed under the following eight headings:

(i) *Experimental conditions*

As Table 1 shows, quite a wide variety of ranges of temperature and pressure have been used for the kinetic studies, and this variety is increased by the alternatives either of the gas phase or the liquid phase as the reaction medium; it might be that it is these variations in experimental conditions, by leading perhaps to a change in the mechanism of the reaction, which are responsible for the observed variations in the Arrhenius parameters.

Against this suggestion, the linearity of the Arrhenius plots indicates that no important changes in mechanism occur over the individual experimental temperature ranges used; again, the first order dependence shows clearly that the total pressure of peroxide and of any additive used in the gas phase decompositions have always been sufficient to maintain the equilibrium concentration of activated molecules corresponding to the Lindemann "high pressure" region. In addition, there is no correlation either for diethyl peroxide or for di-t-butyl peroxide between either the pressure or the temperature range used and the value of E (or $\log A$) obtained—while whereas the overall temperature and pressure ranges covered for these two compounds were quite similar, their Arrhenius parameters are quite distinctly different. As regards the effect of medium, the parameters for the decomposition of di-t-butyl peroxide in various solvents (j, k and l) lie well within the range of those for the gas-phase decomposition; the two other peroxides studied only in solution (t and v) give points which lie very close to the correlation line in Fig. 1. All these facts indicate that the Arrhenius parameters are insensitive to the temperature range, pressure range, and medium in which the decomposition is carried out, and that changes in these cannot be held responsible for the observed variations in the parameters.

(ii) *Misfitting in the Arrhenius plots*

The derivation of Arrhenius parameters from rate constants, k, measured at various absolute temperatures, T, involves fitting a straight line to the plot of $\log k$ against T^{-1}; naturally, there must always be some uncertainty in making this fit because of experimental uncertainties in the values of k and T. If for any given plot the mean point is taken as one through which any acceptable line must pass (as is the case in making a "least squares" fit) then any over-estimate (or under-estimate) of the slope of the line in fitting it to the data will lead to the intercept also being over- (or under-) estimated. Now since E, and $\log A$, are obtained directly from (minus) the slope, and from the intercept, of this plot (compare Eq. (1)), then even random shifts in the line in the fitting will lead to a direct correlation between the corresponding values of E and $\log A$; in fact, as long as the experimental temperature range is small compared with the average absolute temperature,* the "random" correlation has the linear "isokinetic" form:

$$\log A = \log \bar{k} + (E/R\bar{T}) \log e \tag{5}$$

where $\bar{k}$ and $\bar{T}$ are the mean values for the set of experimental results. This type of effect has been pointed out several times before[22–24] as a source of spurious correlations; its occurrence would, in fact, explain why in the present case, the various points for diethyl peroxide and for di-t-butyl peroxide in Fig. 1 lie largely *along* the isokinetic line rather than being strewn randomly, the reason being that the isokinetic temperature, T_i (483°K) is fairly close to the overall average-temperature (433°K). However, the extensive experimental data for these two peroxides demonstrates clearly that even if we ascribe all of the spread in the values for each peroxide to this effect, in actual practice it leads to a standard deviation of only about 1 kcal mole^{-1} in the value of E;

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* For the data in Table 1 the average temperature-range is 35° as compared with the overall average-temperature of 433°K.

[22] O. Exner, *Nature* **201**, 488 (1964).

[23] R. C. Peterson, *J. Org. Chem.* **29**, 3133 (1964).

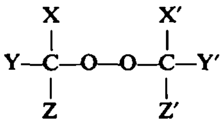
[24] J. E. Leffler, *Nature* **205**, 1101 (1965).

comparison with the overall range of about 9 kcal mole^{-1} shows that the present correlation cannot arise from misfitting in the original Arrhenius plots.

(iii) *True variations in bond dissociation energy*

Since the peroxides in Table 1 are distinct compounds, they would be expected on general grounds to have somewhat different dissociation energies for their peroxide bonds, which would in turn result in varying values of E.

Even so, all of the peroxides in Table 1 can be represented by the basic structure (I), where X, Y, etc. = H, alkyl or phenyl; the variable groups are thus separated by two atoms from the crucial bond, which would effectively insulate it from any electronic effects from these groups, so that changes in their nature would not be likely to affect D(RO—OR′) appreciably; thus, even in the extreme case of di-α-cumyl peroxide ($X = X' = Ph$, $Y = Y' = Z = Z' = Me$), due to the presence of the intervening carbon atom there could be no direct resonance stabilization of the alkoxy radical by the phenyl ring; even if we were to ascribe the reduction in E of about 3 kcal mole^{-1} in going from di-t-butyl peroxide to t-butyl α-cumyl peroxide (t) to an indirect stabilization of the cumyloxy radical, one would expect a further similar reduction in going to di-α-cumyl peroxide (v), whereas no change occurs at all. In fact, the pattern expected is that shown by the series: di-t-butyl peroxide; ethyl t-butyl peroxide; di-ethyl peroxide, where such resonance stabilization, direct or indirect, is completely out of the question.



$$Y-\overset{X}{\underset{Z}{\overset{|}{\underset{|}{C}}}}-O-O-\overset{X'}{\underset{Z'}{\overset{|}{\underset{|}{C}}}}-Y'$$

I

Instead of considering the effect of influences transmitted through bonds, we can consider those from direct steric forces between the R and R′ groups, which will be fairly close together spatially due to the skew configuration of the peroxide bond; such non-bonded repulsions as there are between R and R′ would be expected to lead to reductions in E depending directly on the bulk of these groups, so that the order of E-values for the symmetrical peroxides would be expected to be:

$$PhCMe_2 < Bu^t < Pr^n < Et < Me \qquad (6)$$

which is in strong contrast with the observed order, (4).

It is clear that neither electronic nor steric effects from the substituent groups can give variations in D(RO—OR′) comparable either in size or direction to the observed variations in E. Furthermore, whatever small variations there might be in E, as long as the decomposition is still truly unimolecular the pre-exponential factor A should throughout have the "normal" value of about 10^{13} sec^{-1} ($\log A \simeq 13$),[19] as contrasted with the observed values which range between 10^{12} and 10^{16} sec^{-1}.

(iv) *Initial scission into three fragments*

Studies on the kinetics of the thermal decomposition of the organomercury compounds, RHgR′, have shown[25] that these compounds can be divided into two classes:

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[25] H. V. Carter, E. I. Chappell and E. Warhurst, *J. Chem. Soc.* 106 (1956); H. O. Pritchard, *J. Chem. Phys.* **25**, 267 (1956).

for those in the first ($HgMe_2$, $HgEt_2$, PhHgCl, PhHgBr), A is "normal" in its value (with $\log A = 13{\cdot}8 \pm 0{\cdot}6$) and E can be taken to correspond to the scission in the initial step of the decomposition of one Hg—R bond (i.e. to give R· and R′Hg·); for those in the second ($HgPh_2$, $HgPr^n{}_2$, $HgPr^i{}_2$), A is anomalously high ($\log A = 16{\cdot}0 \pm 0{\cdot}7$) while E corresponds closely to the energy for the dissociation of both the Hg—R and the Hg—R′ bond, which indicates that with this second class of compounds the initial step of the decomposition is the scission into three fragments (Hg + R· + R′·) rather than two.

Clark and Pritchard[26] have extended this interpretation to the apparently similar cases of the dialkyl peroxides, and in particular of diethyl peroxide and di-t-butyl peroxide; they suggest that with diethyl peroxide since A is close to "normal" then the initial step in its decomposition is the simple scission (1), and activation energy E thus corresponds to the dissociation energy of the peroxide bond. However, on the basis of the high values of A and E, for di-t-butyl peroxide, they further suggest that here the initial step of the decomposition is into three fragments, involving scission of the peroxide bond with concurrent scission of one of the alkoxy radicals into an alkyl (methyl) radical and a ketone (acetone):

$$((CH_3)_3CO)_2 \rightarrow (CH_3)_3CO\cdot + (CH_3)_2CO + CH_3\cdot \tag{7}$$

As with the mercury alkyls, the high value for the activation energy would presumably represent that required to break both of the bonds (less that released, in the case of the peroxides, in the concurrent formation of the carbonyl linkage), and the high value of A would reflect the greater probability of accumulating this excess energy within two bonds, rather than only one as in the case of simple two-fragment scission (1). This three-fragment scission is indeed consistent with the products, acetone and ethane, of the vapour phase decomposition of di-t-butyl peroxide (the remaining steps of the mechanism to give these products would be the scission of the remaining alkoxy radical to form the second molecule of acetone and another methyl radical, followed by combination of the methyl radicals). However, this explanation becomes less plausible when examined from the three viewpoints of the products of the decomposition of di-t-butyl peroxide in various solvents, the Arrhenius parameters for the other peroxides, and the actual rate of the decomposition.

First, although in the vapour phase the products of the reaction are solely ethane and acetone, in solution in tributylamine (l) the sole product from the peroxide is t-butyl alcohol, whilst with isopropylbenzene (k) and with t-butylbenzene (j) as solvent the products are mixtures of the ketone and the alcohol, the alcohol predominating with isopropylbenzene and the ketone predominating with t-butylbenzene.[10] Now tributylamine is a very efficient "radical trap", due to its six labile α-hydrogen atoms, whilst isopropylbenzene and t-butylbenzene do have some activity as such traps but are progressively less efficient in this respect; it is clear from the nature of the products that in the liquid phase the initial step must be the simple scission (1) to form two t-butoxy radicals, which in the case of tributylamine as solvent are rapidly converted into t-butyl alcohol by each abstracting a hydrogen atom from the solvent; with the other two solvents a proportion of the t-butoxy radicals decompose into acetone and a methyl radical before they have an opportunity to attack the solvent, and hence

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[26] D. Clark and H. O. Pritchard, *J. Chem. Soc.* 2136 (1956).

some acetone does appear in the products. Since both the actual rates of decomposition and the Arrhenius parameters for the gas phase and the solution decompositions are so closely similar (Table 1), this suggests the mechanisms of their rate determining steps are also the same and that even in the gas phase the initial step is indeed the simple scission (1) followed by a distinct step for the alkoxy-radical decomposition, with the proposed three-fragment scission (7) making little or no contribution.

As regards fitting the other peroxides into this picture, it seems reasonable enough for ethyl t-butyl peroxide (h) to have parameters halfway between those for diethyl peroxide and di-t-butyl peroxide, since only *one* of the alkoxy radicals from it would be susceptible to the concurrent scission; however, it is very surprising to find that di-α-cumyl peroxide (v) and t-butyl α-cumyl peroxide (t) also have these same values, for the α-cumyloxy radical would be expected to be even more susceptible than the t-butyloxy radical to concurrent splitting-off of a methyl radical:

$$(\mathrm{PhC(Me)_2O})_2 \rightarrow \mathrm{PhC(Me)_2O\cdot} + \mathrm{PhC(Me)O} + \mathrm{Me\cdot} \qquad (8)$$

since there is so much resonance stabilization in the acetophenone produced; these two peroxides ought, on the three-fragment scission basis, to have Arrhenius parameters close to those of di-t-butyl peroxide. It is even more surprising to find that dimethyl peroxide (a and b) and dipropyl peroxide (g) have parameters much greater than diethyl peroxide and almost as great as di-t-butyl peroxide; even on energetic grounds one would not expect to get any three-fragment scission with dimethyl peroxide, since this would require a hydrogen atom rather than an alkyl radical to be split off:

$$(\mathrm{CH_3O})_2 \rightarrow \mathrm{CH_3O\cdot} + \mathrm{CH_2O} + \mathrm{H\cdot} \qquad (9)$$

In addition, in the presence of the radical trap nitric oxide the sole product formed is methyl nitrite,[4] presumably arising from addition of the nitric oxide to the methoxy radicals formed in the initial simple scission (1). Again, although the three-fragment scission is formally possible for dipropyl peroxide:

$$(\mathrm{CH_3CH_2CH_2O})_2 \rightarrow \mathrm{CH_3CH_2CH_2O\cdot} + \mathrm{CH_2O} + \mathrm{CH_3CH_2\cdot} \qquad (10)$$

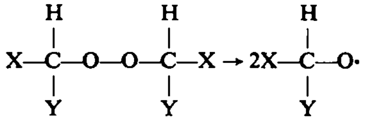
precisely the same holds for diethyl peroxide which has a "normal" value of A; in addition, if reaction (10) occurred to an appreciable extent with dipropyl peroxide it would give appreciable amounts of butane and formaldehyde in the products, whereas the major products seem to be propionaldehyde and propyl alcohol,[9] formed presumably by disproportionation of the propoxy radicals from the initial scission (1).

A final objection arises from the actual *rates* of decomposition. At the isokinetic temperature (210°) all the systems have a common rate constant (0·1 $\mathrm{sec^{-1}}$) and hence the same rate of decomposition at this temperature for a given pressure or concentration of peroxide. In general, the temperatures actually used are somewhat below this, so that the actual rate constants and corresponding rates are highest for the cases with the lowest activation energy; thus, at the overall average-temperature, 160°, the rate constant k for diethyl peroxide is four times that for di-t-butyl peroxide (that the discrepancy is not greater results from the compensating effect of the higher A-factor for di-t-butyl peroxide). Now the simple scission (1) and the three-fragment scission (7) must occur alongside each other, with the total rate that of the sum of the two; for diethyl peroxide the simple scission (1) must be taken by hypothesis to be predominant, but in the case of di-t-butyl peroxide there is no reason to expect there to be any suppression of the simple scission (1), whose rate should be much the same as that for diethyl peroxide at this same temperature. Thus the contradiction arises that the only way in which the three-fragment scission could become predominant with di-t-butyl peroxide would be for its rate constant to be much greater than that for diethyl peroxide, whereas in actual practice it is much less; further, there seems to be no way in which we can reduce the rate of the simple scission with di-t-butyl peroxide (such as by "adjusting" the corresponding value of A or E) without at the same time reducing that of the closely related three-fragment scission to the same extent.

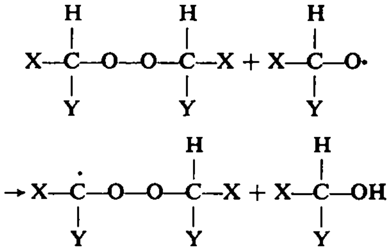
It is clear that these three objections weigh very heavily against invoking varying contributions from a three-fragment scission as the explanation of the behaviour of the Arrhenius parameters.

(v) *Radical-induced decomposition*

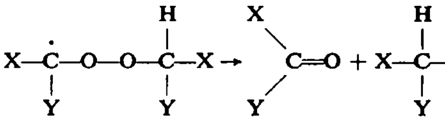
Although, as was indicated at the beginning, most of the present type of peroxides are comparatively resistant to radical-attack, some of them, and particularly the primary alkyl compounds, are not completely resistant; thus one cannot *a priori* rule out the possibility of radical-induced decomposition as an appreciable or even predominant contribution to the overall decomposition. To fit in with the first order behaviour shown experimentally, it would be necessary for this contribution to involve a chain reaction having *two alternating chain carriers*, with the chain termination taking place by their mutual combination (or disproportionation);[27] this is superficially a possibility for the peroxides, for the radical-attack would involve abstraction of an α-hydrogen atom from the peroxide; the two chain carriers would be the alkoxy radical RO· (or R′O·), and that produced by its abstractive attack on the peroxide itself; the cross-interaction would be necessary to terminate the chain, since the recombination of alkoxy radicals would simply produce the peroxide again, and the combination of "peroxide radicals" would be too slow because of their low concentration. The overall mechanism of such a process with a symmetrical peroxide containing an α-hydrogen atom would be:



$$X-\overset{H}{\underset{Y}{C}}-O-O-\overset{H}{\underset{Y}{C}}-X \rightarrow 2X-\overset{H}{\underset{Y}{C}}-O\cdot \qquad (11)$$



$$X-\overset{H}{\underset{Y}{C}}-O-O-\overset{H}{\underset{Y}{C}}-X + X-\overset{H}{\underset{Y}{C}}-O\cdot \rightarrow X-\overset{\cdot}{\underset{Y}{C}}-O-O-\overset{H}{\underset{Y}{C}}-X + X-\overset{H}{\underset{Y}{C}}-OH \qquad (12)$$



$$X-\overset{\cdot}{\underset{Y}{C}}-O-O-\overset{H}{\underset{Y}{C}}-X \rightarrow \overset{X}{\underset{Y}{>}}C{=}O + X-\overset{H}{\underset{Y}{C}}-O\cdot \qquad (13)$$

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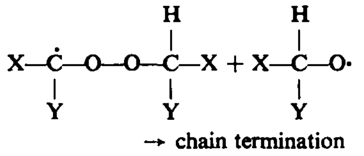
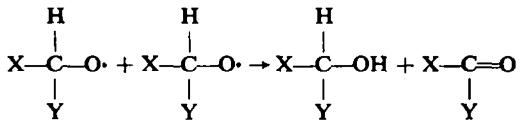
[27] A. A. Frost and R. G. Pearson, *Kinetics and Mechanism* 2nd ed., p. 252. John Wiley, New York (1961).



$$X-\overset{\bullet}{\underset{Y}{C}}-O-O-\overset{H}{\underset{Y}{C}}-X+X-\overset{H}{\underset{Y}{C}}-O\cdot \quad (14)$$
$$\rightarrow \text{chain termination}$$

The chain thus would involve the alternation of reactions (12) and (13); its driving force would arise from the greater case of decomposition of the peroxide-radical in (13) compared with that of the peroxide itself in (11). This overall process would give the observed first-order dependence of the rate of decomposition of the peroxides, with overall rate constant giving Arrhenius parameters in general appreciably different from that of the simple scission reaction, so that varying contributions from the two possibilities with peroxides having different substituent groups would be expected to give variations in A and E.

The weakness of this mechanism is that to obtain the observed first order dependence, the rate of the cross-termination process (14) must be greater than that of the disproportionation of alkoxy radicals:



$$X-\overset{H}{\underset{Y}{C}}-O\cdot+X-\overset{H}{\underset{Y}{C}}-O\cdot \rightarrow X-\overset{H}{\underset{Y}{C}}-OH+X-\underset{Y}{C}{=}O \quad (15)$$

So long as we say that the α-hydrogen atom on the peroxide is liable to abstraction by an alkoxy radical in reaction (12) (and this is of course a crucial step in the chain reaction), then we must also accept the similar abstraction reaction (15) into the overall scheme. If reaction (15) occurs at all rapidly, it will reduce the alkoxy radical concentration to such a low level that the simple fission (11) becomes rate determining; even if it occurs at only a moderate rate, it may displace (14) as the predominant termination process, so that the chain process would be *three-halves* order, in conflict with the experimentally observed first-order nature of the overall decomposition. Further, the activation energy of the decomposition reaction analagous to (13) for the diethyl ether radical[16] is only about 24 kcal mole^{-1}, which is at least 60 kcal mole^{-1} less than that for normal C—O bond fission; even only half this reduction in activation energy in the case of the peroxide radical would lead to reaction (13) having zero activation energy and to (12) and (13) occurring essentially simultaneously, so that the concentration of peroxide radicals could not reach an appreciable level, and disproportionation of alkoxy radicals would become the sole process for chain termination.

In addition, when we apply this proposed mechanism to the actual peroxides, it is clear that such a chain decomposition mechanism is not a possibility with any of the tertiary peroxides, since they do not possess the necessary α-hydrogen atoms;* thus such a mechanism does explain the differences in Arrhenius parameters between the

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* Radical-induced decomposition by attack on the peroxide oxygen atoms does not seem to occur with peroxides—thus for the decomposition of pure liquid di-t-butyl peroxide (E. R. Bell F. F. Rust and W. E. Vaughan, *J. Amer. Chem. Soc.* **72**, 337 (1950)) the radical attack on the peroxide occurs on the *methyl hydrogens*, leading to isobutylene oxide in the final products; the susceptibility of hydroperoxides to radical attack can be explained by hydrogen-abstraction from the hydroperoxide group, and that of the diacyl peroxides by attack on the *carboxyl* oxygen.

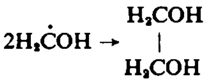
tertiary peroxides, nor the fact that they lie on a common line, in Fig. 1, with the primary peroxides, for which such chain decomposition is superficially feasible.

Even discounting that the overall decompositions are strictly first order for these primary compounds, the available evidence from the effect of additives on the rate of the reaction, and from the products of the reaction, suggests that the actual contribution from such radical-induced decomposition is quite small.

Thus, in the case of dimethyl peroxide, the kinetic measurements of Takezaki and Takeuchi[3] (a) were carried out using a large excess of methanol vapour, which must have effectively suppressed any radical-induced decomposition by converting methoxy radicals into the much less active hydroxy-methyl radicals:

$$CH_3O\cdot + CH_3OH \rightarrow 2H_2\dot{C}OH \tag{16}$$

and this is confirmed by the appearance of ethylene glycol, formed in (17), as the major product:



$$2H_2\dot{C}OH \rightarrow \begin{matrix} H_2COH \\ | \\ H_2COH \end{matrix} \tag{17}$$

Indeed, the rate constant at 167° was the same in the absence of methanol vapour as in its presence,[3] which suggests that even in the absence of such a radical trap (as in the study by Hanst and Calvert[4]) there is no appreciable amount of radical-induced decomposition.

With diethyl peroxide, the attempt by Rebbert and Laidler[7] to remove free radicals as they were formed and hence suppress any chain processes by carrying out the decomposition in the presence of an excess of toluene vapour, was patently unsuccessful, since if the toluene had acted efficiently by reacting with the radicals to form the much less active benzyl radical, large amounts of dibenzyl should have been produced, whereas only traces were obtained in the actual experiments; however, the pressures of peroxide used in this study were so low (*ca.* 0·1 torr) that chain processes, involving as they do the bimolecular attack of alkoxy radicals on peroxide, (12), must have been slow compared with unimolecular decomposition of these radicals, and this is supported by the formation of ethane and formaldehyde as the major products, presumably *via* the sequence:

$$(C_2H_5O)_2 \rightarrow 2C_2H_5O\cdot \tag{18}$$

$$C_2H_5O\cdot \rightarrow CH_3\cdot + CH_2O \tag{19}$$

$$2CH_3\cdot \rightarrow C_2H_6 \tag{20}$$

as contrasted with the products, ethanol and acetaldehyde, to be expected from the chain sequence (11) through (14).

It is important to note that the effect of additives such as nitric oxide[5,6,8], cyclohexene,[8] and iodine,[8] in apparently inhibiting the decomposition of diethyl peroxide, and apparently thus providing evidence for radical-induced chain decomposition, is misleading; in the first place, nitric oxide is known[28] to react rapidly with diethyl peroxide in the dark, at room temperature, to form ethyl nitrite:

$$(C_2H_5O)_2 + 2NO \rightarrow 2C_2H_5ONO \tag{21}$$

[28] H. N. Mortlock and D. W. G. Style, *Nature* **170**, 706 (1952).

More importantly, these studies[5,6,8] used pressure changes as criteria of the occurrence of reaction; it is clear that even when nitric oxide, cyclohexene or iodine simply act as radical traps towards the ethoxy radicals formed in the initial scission, there will be no overall change of pressure, e.g. with cyclohexene, the overall process is:

$$(C_2H_5O)_2 + 2C_6H_{10}\ \text{(cyclohexene)} \rightarrow 2C_2H_5OH + (C_6H_9)_2\ \text{(bicyclohexenyl)} \qquad (22)$$

and hence one would not *expect* there to be any pressure change in the presence of these substances; this, of course, provides no evidence for or against chain decomposition, but it is still consistent with simple scission (1) as the rate determining step for diethyl peroxide in the absence or presence of such additives.

There seems no direct evidence in the case of dipropyl peroxide for or against chain decomposition, since the products (propyl alcohol and propionaldehyde) are equally consistent either with chain decomposition or with simple scission followed by disproportionation of the resultant propoxy radicals; however, the low pressures of peroxide (0·2–3 torr) used in the study by Harris[9] (g) would, as with diethyl peroxide, have militated against any appreciable amount of chain decomposition.

Thus, despite the lack of full confirmatory evidence, the first order dependence experimentally observed and the reaction products strongly suggest that radical-induced chain decomposition does not make an important contribution to the rate of thermal decomposition of the primary dialkyl peroxides.

(vi) *Molecular mechanisms*

The majority of the mechanisms proposed for the thermal decomposition of peroxides involve the production of free radicals; there are, however, many cases of decomposition of organic molecules where free radicals are not involved, the mechanism being simply a re-arrangement of the molecule or its splitting into two or more valence-satisfied molecules. The principle argument against this being a possibility with the organic peroxides, is that their decompositions are good sources of free radicals, and that in the cases noted previously where the decomposition has been carried out in the presence of an efficient radical trap, there is invariably almost complete conversion of the peroxide into the products to be expected from interaction between the trap and the corresponding alkoxy radicals. In addition, a molecular mechanism, involving as it would the concerted motion of the atoms in the molecule, is more likely for this very reason to have a low value for A, rather than the anomalously high value for this parameter which is a feature for many of the peroxides.

(vii) *"Loosening" in the transition state*

It has been suggested[29,30] that the anomalously high values of the pre-exponential factor, A, for the decomposition of peroxides arises from there being a greater rotational freedom in the transition state which would thus favour the formation of this state. Arguments of this kind, based on considerations of the configurations and vibrations of a molecule in a reaction transition state, are necessarily somewhat metaphysical, since this state is by definition the most transient in the whole decomposition process. However, in the simplest picture this state is a vibrationally excited state of

[29] D. E. Hoare, J. B. Protheroe and A. D. Walsh, *Trans. Faraday Soc.* **55**, 548 (1959).

[30] M. Szwarc, *Discuss. Faraday Soc.* **14**, 125 (1953).

the molecule, with the excitation confined to the peroxide linkage and with the activation energy appearing as a greater amplitude for its stretching mode. Now the repulsions between non-bonded atoms in a molecule are much more increased by bringing such atoms closer together than they are decreased by moving these same atoms apart the same amount; thus the increase in repulsive forces between the substituent groups R and R′ on the compressive half of the vibration of peroxide bond would more than outweigh the relief on the expansive half; if we take it that rotational restriction arises from such forces, there ought in fact to be *greater* restriction to rotation in the transition state than in the normal state. Thus, if anything, the A values ought to be abnormally low, rather than abnormally high, if this effect were an important feature of the transition state.

(viii) *Energy of activation spread out among a number of vibrational modes*

On the simplest view, the activation energy of the transition state is taken to be concentrated in the vibration of the bond to be broken, i.e. the peroxide bond. However, the vibration of this bond is coupled to those of the other bonds in the molecule, and it is possible that some of these are involved in supplying the activation energy to the critical bond. In this case the fraction of molecules activated in a suitable fashion with energy in excess of a value, ε, becomes greater than the simple Boltzmann factor; if the number of effective vibrational modes is n, then this fraction, $\mathrm{f}(\varepsilon)$, becomes:[31]

$$\mathrm{f}(\varepsilon) = \exp(-\varepsilon/RT)\{(\varepsilon/RT)^m/m! + (\varepsilon/RT)^{m-1}/(m-1)! + \ldots\} \tag{23}$$

where

$$m = n - 1 \tag{24}$$

so that the rate constant of the bond-scission is given by:

$$k = \nu\mathrm{f}(\varepsilon) \tag{25}$$

where the "frequency factor" ν lies between the greatest and the least of the vibrational frequencies of the whole molecule,[32] i.e. *ca.* 10^{13} sec^{-1}. Provisionally identifying ε with the experimentally determined activation energy, the factor (ε/RT) for the peroxide data (Table 1) lies between the extreme limits of 24 and 51, with a mean value of 35; thus for most purposes, we need retain only leading term of the sum in Eq. (23) so that Eq. (25) becomes:

$$k = \nu\{(\varepsilon/RT)^m/m!\}\exp(-\varepsilon/RT) \tag{26}$$

Bearing in mind that the experimental activation energy is obtained from the slope of the plot of $\log k$ against $1/T$, if we equate the values of $\mathrm{d}(\log k/\mathrm{d}(1/T))$ from Eqs. (2) and (24) we obtain:

$$E = \varepsilon - mRT \tag{27}$$

and similarly, since $\log A$ is the intercept of this same plot, we obtain:

$$\log A = \log \nu + m \log(\varepsilon/eRT) - \log m \tag{28}$$

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[31] C. N. Hinshelwood, *Proc. Roy. Soc.* (London) **113**, Series A, 230 (1926); R. H. Fowler and E. K. Rideal, *Proc. Roy. Soc.* (London) **113**, Series A, 570 (1926).

[32] N. B. Slater, *Proc. Roy. Soc.* (London) **194**, Series A, **112** (1948).

and with (ε/RT) having the limits stated above, $\log(\varepsilon/eRT)$ has a value very close to unity (strictly, 1·1 ± 0·2), so that Eq. (29) can be written:

$$\log A = \log \nu + m - \log m \tag{29}$$

Comparing Eqs. (27) and (29), it is clear that E is decreased by about 1 kcal mole^{-1} for each unit increase of m (the actual value of RT lies within the limits 1·00 ± 0·25 kcal mole^{-1} for the range of T in Table 1) while $\log A$ is increased by about one unit for the same change. This is incompatible with the *positive* correlation observed between $\log A$ and E, which indicates that such various degrees of coupling between the vibrational modes, and contributions from extra vibrational modes, upon changes in the structure of the peroxide, cannot explain the variations in the Arrhenius parameters.

Concluding remarks

It is clear from the preceding discussion that the weight of the evidence is in favour of the simple scission (1) of the peroxides set out in Table 1 as the rate determining step in their thermal decomposition, and that neither three-fragment scission, chain decomposition, nor a molecular mechanism makes an appreciable contribution; at the same time, the observed variations in E cannot be related to real variations in the dissociation energy of the peroxide bond, those in A cannot be ascribed to "loosening" in the transition state of the decomposition, while the isokinetic correlation between the two parameters cannot be explained either by misfitting in the Arrhenius plot or by varying contributions from vibrational modes in supplying activation energy to the —O—O— bond in the transition state.

This situation is rather disturbing, since peroxides are *the* class of compounds to be expected to decompose in a simple unimolecular fashion, with a pre-exponential factor of close to 10^{13} sec^{-1} and the activation energy representing the (essentially constant) dissociation energy of the peroxide bond, for their structure is such that their highly labile peroxide bond is effectively isolated from effects from the remainder of the molecule.

It is difficult to see any way in which the phenomena outlined here can be explained, since the approaches discussed seem to exhaust all the plausible explanations. Even with regard to the topic which was the starting point for the discussion, i.e. the dissociation energy of the peroxide bond, the most that can be suggested is that the alternative direct method available for polyatomic molecules, that of electron impact,[33] should be applied to these compounds to determine D(RO—OR′) and compare it with the values of E from the kinetic method; in the meantime, there must be a suspension of judgement on what is the correct value for this bond dissociation energy.

[33] Ref. 1, chap. 2.