A Study of the Thermal Decomposition of Allyl t-Butyl Peroxide and 3-Hydroperoxy-1-Propene (Allyl Hydroperoxide) in Toluene.

BY

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Brock University, August 1976
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To
Leela and Usha.
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ABSTRACT

Kinetics and product studies of the decompositions of allyl-t-butyl peroxide and 3-hydroperoxy-1-propene (allyl hydroperoxide) in toluene were investigated. Decompositions of allyl-t-butyl peroxide in toluene at 130-160° followed first order kinetics with an activation energy of 32.8 K.cals/mol and a log A factor of 13.65. The rates of decomposition were lowered in presence of the radical trap methyl styrene. By the radical trap method, the induced decomposition at 130° is shown to be 12.5%. From the yield of 4-phenyl-1,2-epoxy butane the major path of induced decomposition is shown to be via an addition mechanism. On the other hand, di-t-butyl peroxyoxalate induced decomposition of this peroxide at 60° proceeded by an abstraction mechanism. Induced decomposition of peroxides and hydroperoxides containing the allyl system is proposed to occur mainly through an addition mechanism at these higher temperatures. Allyl hydroperoxide in toluene at 165-185° decomposes following 3/2 order kinetics with an $E_a$ of 30.2 K.cals per mole and log A of 10.6. Enormous production of radicals through chain branching may explain these relatively low values of $E_a$ and log A. The complexity of the reaction is indicated by the formation of various products of the decomposition. A study of the radical attack of the hydroperoxide at lower temperatures is suggested as a further work to throw more light on the nature of decomposition of this hydroperoxide.
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Introduction:

Peroxides and hydroperoxides in Chemistry.

Molecules with bond energies of 25-35 Kcals should be useful radical initiators at a temperature of 50-150°C. Although several organic compounds meet this requirement, by far the most commonly used are those containing the O-O bond. Organic hydroperoxides and peroxides are useful initiators for free radical chain reactions. A number of peroxides and hydroperoxides have been examined as initiators for free radical polymerisation of styrene. The hydroperoxides were of relatively low efficiency as initiators in comparison with peroxides. It appears that the former have a tendency to undergo secondary decompositions.

Organic hydroperoxides and peroxides are also of much interest to organic chemists as they are intermediates in the autoxidation of hydrocarbons. The mechanism of autoxidation is well known:

\[ R. + O_2 \rightarrow RO_2. \]

\[ RO_2. + RH \rightarrow RO_2H + R. \]

It is clear that hydroperoxide accumulates during the chain process. This leads to initiation caused by an energetically favourable hydroperoxide decomposition. Thus as hydroperoxide
yield increases, the rate of initiation and hence the rate of autoxidation will increase giving the familiar initial autocatalytic rates of oxygen absorption for self initiated autoxidations. (3)

Hydroperoxides and peroxides are also useful as radical initiators in the autoxidative degradation method for the chemical characterisation of polymers (4). A hydrocarbon polymer is converted to a polymeric hydroperoxide by means of a radical initiator and the polymeric hydroperoxide undergoes secondary decompositions resulting in an autocatalytic process.

**Mechanisms of decomposition of peroxides and hydroperoxides.**

Hydroperoxides and peroxides may be decomposed photolytically or by metal ions. (5,6)

\[
\text{RO}_2\text{H} \xrightarrow{\text{hv.}} \text{RO} + \cdot\text{OH} + \cdot\text{OR}
\]

\[
\text{Fe}^{2+} + \text{RO}_2\text{H} \xrightarrow{} \text{RO} + \text{Fe}^{3+} + \cdot\text{OH}^{-}
\]

However this discussion will be concerned with thermal mechanisms only, starting with unimolecular homolysis.

\[
\text{RO}_2\text{H} \xrightarrow{} \text{RO} + \cdot\text{OH} + \cdot\text{OR}
\]

This process occurs to some extent in nearly all thermal reactions and frequently predominates. In many cases,
however, it is obscured by competing reactions. Thus knowledge of the expected activation energy for unimolecular homolysis serves as a useful test of mechanism in situations encountered experimentally. If the activation energy for the reverse reaction of the thermal homolysis (combination of two radicals) is zero, then the activation energy for the forward reaction is equal to the bond energy of O-O bond, $D_{0-0}$.

Calculation of $D_{0-0}$ for peroxides and hydroperoxides from thermochemical data is non-reliable as they are thermally unstable, and are difficult to obtain in very pure form. Both of these kinds of difficulties are minimal in the case of t-Bu$_2$O$_2$ and maximal in n-alkyl hydroperoxides. From the experimentally determined and reliable values of heats of formations of t-Bu$_2$O$_2$ and hydrogen peroxide, and by the use of the rule of additivity of group properties, Benson showed that heat of formation of ROOH should be the average of the heats of formation of ROOR and HOOH. From this Benson calculated $D_{0-0}$ (ROOH) as 42 - 44 kcal as $\text{which is the average of } D_{\text{RO-OR}}$ and $D_{\text{HOOH}}$. $D_{0-0}$ (ROOR) is calculated to be 38-39 kcal.

A number of studies have been done on the thermal decomposition of dialkyl peroxides. Most of the investigations were done on di-tert-butyl peroxide, the most well behaved member of the class. Decomposition of dialkyl peroxides in general proceeds via simple unimolecular homolysis; but there are exceptions.

Raley et al studied the thermal de-
composition of \( t-Bu_2O_2 \) and di-t-amyl peroxide in the vapor phase. Decompositions of the former followed first order kinetics. The use of chain inhibitors did not affect the reaction velocity appreciably. The experimentally determined activation energy, \( 39.1 \pm 0.5 \) K.cals/mol was close to the \( D_{O-O} \) of the peroxide, 39 K.cals. However, while the decomposition of di-t-amyl peroxide at 130-150\(^\circ\)C is approximately first order, the rate constant was pressure dependent, indicative of contributions from a higher order process. The investigation of the decomposition of \( t-Bu_2O_2 \) was extended to studies in solvents like cumene, t-butyl benzene, and tri-n-butyl amine. Decompositions in these solvents were first order processes with the rates and activation energies nearly equal to those in the vapor phase. Thus Raley et al concluded that homolysis of \( O-O \) bond was the rate determining step in the decompositions of \( t-Bu_2O_2 \). 

\[
\text{t-Bu}_2O_2 \rightarrow 2 \text{t-BuO}.
\]

Subsequent reactions of the tertiary alkoxy radicals like \( t-BuO \) include both H-abstraction (equation 1) and \( \beta \)-scission (equation 2).

\[
\begin{align*}
t-BuO. + RH & \xrightleftharpoons[ka]{k_d} t-BuOH + R. & (1) \\
t-BuO. & \xrightarrow{k_d} Me_2CO + Me. & (2)
\end{align*}
\]

Walling and Wagner's study of the solvent effect on the relative rates of H-abstraction and \( \beta \)-scission.
(k_a/k_d ) has shown that this ratio roughly paralleled solvent polarity (11). They concluded that t-BuO_. radicals are solvated and must lose much of its solvation in the transition state for H-abstraction but not in the transition state for β-scission.

Primary and secondary di-alkyl peroxides show another type of decomposition in competition with the usual homolysis. This is the formation of hydrogen by a concerted path (12,13).

\[
\begin{align*}
R' & \ 
\ \ C \ 
\ \ H \ 
\ \ H \ 
\ \ C \ 
\ \ O \\
R & \ 
\ \ O \\
& \ 
\ \ R
\end{align*}
\]

\[\rightarrow 2 \ R \ R' \ C=O + H_2\]

A wide range of activation energies have been reported for thermal decompositions of alkyl hydroperoxides(14,15). But only a few studies have been reported where the activation energy is greater than 40 K\text{cals/mol.} (i.e. close to Benson's bond energy D_{0-O} for ROOH.) Decomposition of t-butyl hydroperoxide in benzene has been reported to show a ΔH of 40.8 K\text{cals/mol.} (16). Very low pressure pyrolysis of t-butyl hydroperoxide over a temperature range of 300-900° showed that the homolysis of the hydroperoxide is in excellent agreement with a 43 K\text{cal} O=O bond (17). Hiatt and Irwin investigated the thermal decomposition of t-BuOOH in
aromatic solvents. At initial concentrations less than 0.2M in toluene, decompositions at 170-180° were first order and largely proceeded by a true homolysis of the O-O bond. The rate constant for the homolytic cleavage of the O-O bond at 170-215° is about $10^{15.8} e^{-43000/RT}$. But the results at 100° in toluene showed that the apparent first order rate constant for the decomposition was twenty times that extrapolated from decompositions at 170-190°. This finding has not been satisfactorily explained.

Another type of decomposition observed in hydroperoxides is the molecularly assisted homolysis caused by polar species like olefins, alcohols, amines, carbonyl compounds, acids, and even other hydroperoxide molecules.

\[
\text{ROOH} \rightarrow \text{S} \rightarrow \text{RO} \rightarrow (\text{SOH})
\]

Evidence of such a phenomenon is the observation that the rate of initiation of styrene polymerization by t-BuOOH is much faster than that calculated from the rate of unimolecular decomposition of the hydroperoxide in inert solvents. Apparently styrene causes the decomposition of the hydroperoxide by molecularly assisted homolysis.

Decomposition of hydroperoxides is often complicated by free radical induced decomposition, co-
monly known as induced decomposition. One type commonly observed for hydroperoxides is

\[
\text{ROOH} + \text{RO.} \rightarrow \text{ROO.} + \text{ROH}
\]

\[
2 \text{ROO.} \rightarrow 2\text{RO.} + \text{O}_2
\]

In solution the radical \text{RO.} may be produced in the solvent cage and has to diffuse out of the cage for propagating a chain. \text{RO.} radicals can terminate in the solvent cage by combination

\[
2 \text{RO.} \rightarrow \text{ROOR}
\]

The diffusion of alkoxy radicals from the cage depends on the viscosity of the medium. Thus the chain length which is the number of propagating steps caused by each initiating radical depends on the viscosity of the medium. The chain length will also be affected by the formation of alkyl radicals either by \(\beta\)-scission or from the solvent and their consequent reaction with oxygen to produce non-radical products as shown. (20,21)

\[
\text{Me.} + \text{ROO.} \rightarrow \text{ROOMe}
\]

\[
\text{CH}_3^* + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2^*
\]
Another type of radical induced decomposition is the free radical displacement on the relatively weak O-O bond of the hydroperoxide.

\[
\text{ROOH} + \text{S.} \rightarrow \text{ROS} + \cdot\text{OH}
\]

\[
\text{ROOH} + \text{S.} \rightarrow \text{SOH} + \text{RO}.
\]

Only a few examples of this type of reaction have been reported (22).

Thermal decompositions of primary and secondary hydroperoxides also show orders higher than first, indicative of induced radical chains (23,24). They differ from the tertiary hydroperoxides in two respects: firstly interaction of two primary or secondary peroxy radicals is faster than for two \(\text{t-BuO}_2\cdot\) radicals and is always terminating; secondly abstraction of hydrogen atom makes \(\cdot\text{OH}\) radical the chain carrier (25,26).

\[
2 \text{RR'}\text{CHO}_2 \cdot \rightarrow \text{RR'}\text{C}=\text{O} + \text{RR'}\text{CHOH} + \text{O}_2
\]

\[
\text{RR'}\text{CHOOH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{RR'}\text{C}-\text{OOH} \rightarrow \text{RR'}\text{C}=\text{O} + \cdot\text{OH}
\]
The contribution from the latter reaction is negligible in the di-t-butyl peroxyoxalate (DBPO) induced decomposition of these hydroperoxides in benzene at 45°C. (27)

Dialkyl peroxides are also subject to free radical induced decomposition, although generally much less sensitive than hydroperoxides to radical attack. Thus thermal decomposition of neat di-t-butyl peroxide gives isobutylene oxide by the following mechanism (28).

\[
\text{Me}_3\text{C}-\text{O}-\text{O-CMe}_3 + \text{RO.} \rightarrow \text{Me}_2\text{C} -\text{O} - \text{O-CMe}_3 + \text{ROH} \\
\text{CH}_2 \\
\downarrow \\
\text{Me}_2\text{C} - \text{C} - \text{CH}_2 + \text{Me}_3\text{CO.}
\]

Decompositions of t-Bu_2O_2 in alcohols and benzyl ethers have been reported to show SH^2 displacement (29,30).

\[
t\text{-}\text{Bu}-\text{O}_2\text{-t-Bu} \rightarrow \text{t-BuOH} + \text{C}=\text{O} + \text{t-BuO.}
\]
Allylic peroxides and hydroperoxides.

Although a number of investigations have been done with peroxides and hydroperoxides, those on allylic peroxides and hydroperoxides are few. Studies on allylic peroxides and hydroperoxides are important since olefins readily autoxidise to give these compounds. They further undergo primary and secondary decompositions. The distinctive features of olefin autoxidation can be seen in the following mechanism of autoxidation of 2-butene. (The stereochemistry of the molecule is neglected in the following equations.)

\[
\text{Initiator} \rightarrow 2 \text{R.} \\
\text{R.} + O_2 \rightarrow \text{RO}_2^* \\
\text{RO}_2^* + \text{CH} \rightarrow \text{RO}_2\text{H} + \text{CH} \\
\text{CH} + O_2 \rightarrow \text{CH}_2\text{O}_2^* 
\]
Addition or Abstraction.
All peroxy radicals $\longrightarrow$ non-radical products $\pm O_2$.

Van Sickle et al studied the peculiarities of olefin autoxidation using well behaved radical initiators, such as ABN. For such radical initiated autoxidations: (31,32)

$$\text{Rate} = \frac{-dO_2}{dt} = k(R_i)^{1/2} (\text{Olefin}).$$

$$R_i = \text{Rate of initiation}.$$

but for the autocatalytic part of the autoxidation where the initiator is the intermediate allylic hydroperoxide:

$$\text{Rate} = k (R_{O_2H}) (\text{Olefin}).$$

In such cases the rate of initiation is several orders of magnitude faster than that feasible for a simple homolysis of the hydroperoxide. The measured apparent 'Ki' has abnormally low activation energy and A factor. Bimolecular initiation of the hydroperoxide was postulated for initiations of these autoxidations:

$$2 R_{O_2H} \longrightarrow R_O + R_{O_2} + H_2O.$$

The early studies on the allylic peroxides and hydroperoxides by Bateman and Hughes (33) are significant. They investigated the decomposition of cyclohexenyl hydroperoxide in cyclohexene and other solvents. In cyclohexene at 80° the decomposition followed an order of 1.77. This 'bimolecular' decomposition appeared to be
in accord with the bimolecular production of initiating free radicals.

More recently Van Sickle has studied the decomposition of 3-hydroperoxy-1-cyclopentene in cyclopentene (34). This decomposition also follows second order kinetics.

On the other hand, Kossovskii et al has found that the decompositions of 2-hydroperoxy-3-butene and crotyl hydroperoxide in t-BuOH at 110-120° follow first order kinetics (35, 36). However the activation energy for decomposition was only 15 K. cals/mol, so that the apparent simplicity of the kinetics is misleading.

As Hiatt and Mc Carrick (37) have most recently pointed out, attempts to relate measurements on gross rates of hydroperoxide decomposition to measurements of gross rates of free radical production require a good deal of caution. Although rates of initiations by allylic hydroperoxides in autooxidising olefins are faster than predicted for unimolecular homolysis, the gross rate of hydroperoxide disappearance in olefinic solvents, (in the absence of O₂, of course), is considerably faster still. Thus the kinetic order of hydroperoxide decomposition is not necessarily related to the kinetic order for free radical production. Indeed, both apparent kinetic orders for initiation as well as for decomposition may be artifacts resulting from a complex set of competing reactions.

Studies on the decomposition of 3-hydroperoxy-2,3-dimethyl-1-butene have demonstrated this possibility (37). Hiatt et al concluded that the main radical producing reaction
involved a chain branching step

\[
\text{RO}_2^+ + \text{ROOH} \rightarrow \text{RO} + \text{R'O} + \cdot \text{OH}
\]

which kinetic analysis showed to be nearly second order in the hydroperoxide. This new theory needs further testing as their conclusions were tentative and their data were insufficient to explain the whole theory. It seemed desirable to study simple allyl hydroperoxide itself. In this case there is no complication from the well known allylic rearrangement (38) and the products should be relatively simpler than from 3-hydroperoxy-2,3-dimethyl-1-butene. Allyl-t-butyl peroxide was chosen as a useful comparison.

The present work constitutes a study of the thermal decompositions of 3-hydroperoxy-1-propene (allyl hydroperoxide) and allyl-t-butyl peroxide in toluene and the conclusions that may be drawn from the results.
Experimental:–

**Instruments used in this work**

The N.M.R. spectra were recorded on either a Brucker WP60 FT N.M.R. spectrometer tuned for H at 60 M.Hz. with a sweep width of 750 Hz. from TMS or a Varian A-60 N.M.R. spectrometer with a sweep width of 500 Hz. from T.M.S. and a sweep time of 250 sec. The I.R. analyses were done using a Perkin Elmer 237B Infrared Spectrophotometer. All mass spectra and G.C. mass spectra were recorded on an A.E.I. MS 30 double beam mass spectrometer which is interfaced to a Pye gas chromatograph.

All G.L.C. analyses were performed on a F & M 700 Laboratory Gas Chromatograph (thermo-conductivity detector) equipped with a Honeywell recorder having a disc integrator and a HP 3370B electronic digital integrator. This Chromatograph is also connected to a vacuum line through a 10 ml U-shaped loop for introducing gas samples. The carrier gas used was helium. A Varian 700 gas chromatograph was used for preparative G.C. work. The F&M 700 chromatograph was also equipped with a F &M power proportionator.

**Reagents and materials.**

a) Those purchased and used. (see table 1)

b) Those synthesised.

1. **Preparation of allyl methyl sulfonate.**

Allyl methyl sulfonate was prepared following the method of Dykstra and Mosher (39). B.P. 70-72° at 3 mm Hg
<table>
<thead>
<tr>
<th>Chemical</th>
<th>Source</th>
<th>Purification step</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allyl alcohol</td>
<td>M.C.B. Co.</td>
<td>Distillation</td>
</tr>
<tr>
<td>Methane sulfonyl chloride</td>
<td>Eastman Kodak Co.</td>
<td>----</td>
</tr>
<tr>
<td>t-BuOOH.</td>
<td>Lucidol Co.</td>
<td>Distillation under reduced pressure.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Distillation</td>
</tr>
<tr>
<td>Allyl bromide</td>
<td>Aldrich Chemicals</td>
<td>----</td>
</tr>
<tr>
<td>Disodium E.D.T.A.</td>
<td>Fisher Chemicals.</td>
<td>----</td>
</tr>
<tr>
<td>30% ( \text{H}_2\text{O}_2 )</td>
<td>B.D.H. Chemicals.</td>
<td>----</td>
</tr>
<tr>
<td>Spectroquality toluene.</td>
<td>M.C.B. Co.</td>
<td>Distillation</td>
</tr>
<tr>
<td>Acrolein.</td>
<td>Aldrich Chemicals.</td>
<td>----</td>
</tr>
<tr>
<td>Methanol.</td>
<td>Commercial.</td>
<td>Distillation over disodium E.D.T.A.</td>
</tr>
</tbody>
</table>
Yield. 20%.

N.M.R. analysis of allyl methyl sulfonate.

In CDCl₃ the peaks were at 3.1 δ (CH₃ singlet), 4.6 δ (CH₂O doublet), and 5-6.5 δ (CH=CH multiplet).

Conversion of allyl methyl sulfonate into allyl-t-butyl peroxide.

The method followed was essentially that of Mosher(40)

Allyl methane sulfonate (13.6 gms.), t-butyl hydroperoxide (9 gms.), and methanol (60 ml.) were introduced into a 500 ml round bottom flask, which was cooled in an ice salt bath. The solution in the flask was stirred with a teflon-coated magnetic stirrer. Potassium hydroxide (5.6 gms.) was dissolved in 11.2 ml. of water and added to the stirred solution within a period of 15 min. The reaction mixture was allowed to warm to room temperature gradually and left for 5 hrs. t-Butyl hydroperoxide (2.25 gms) was added to the reaction mixture after a period of 5 hrs. The reaction mixture was then stirred for 15 hrs. The precipitated potassium methane sulfonate was filtered off. The filtrate was extracted several times with 20 ml. portions of pentane. The combined pentane extract was washed three times with 50% KOH and then with distilled water until the water extract was neutral. The pentane extract was then dried with anhydrous sodium sulfate and most of the solvent was removed by distillation at a pressure of 30 mm of Hg using an 8" column packed with pyrex glass helices. The residual liquid which still contained a small quantity of the solvent, was then purified by gas chromatography using an 8', 20% diisodecyl phthalate on Chromosorb W. column. Column temperature (C.T.) 50°, Flow rate 40 ml/min, Retention time (R.T.) of peroxide 13 min. nD 1.4040 (reported nD 1.4015) (41)
The peroxide was found to be 98% pure from G.L.C. and N.M.R. analyses. I.R. and Mass spectra of the peroxide were taken to identify the peroxide. Yield 12%.

**N.M.R. Analysis**

In CDCl₃ the peaks were at 1.1 d (CMe₃ singlet), 4.2 d (CH₂-O doublet) and at 4.8-6.3 d (CH=CH multiplet).

**I.R. Analysis**

In CC1₄ the main bands observed were (in cm⁻¹)
815 (characteristic of C-O-O), 880, 1200, 1250, 1365,1385 (-CMe₃, CH deformation), 1425, 1475, 1650 (C=O stretching), 2950, 2975 and 3080 (C-H stretching).

**Mass spectral analysis.**

The peroxide was stable towards mass spectral analysis. Important peaks and their normalised intensities are given below. (A small peak appeared at m/e 149 which may be due to the impurities in the peroxide.) m/e 28 (100% CH₂-CH₂⁺), m/e 41 (85% CH₂-CH=CH₂⁺), m/e 57 (54% CMe₃⁺), m/e 59 (87% Me₂CO-H⁺), and m/e 130 (7% parent ion).

**A simpler way of preparing allyl t-butyl peroxide.**

The yield of allyl methyl sulfonate was consistently poor due to its decomposition during distillation. An attempt to prepare the peroxide by the following method was found to be very successful.

Freshly distilled t-BuOOH (22.5 gms.) was placed in a 500 ml round bottom flask. A teflon-coated magnetic stirrer was used for stirring. Methanol (30 ml.) was added to the reaction
flask followed by freshly distilled allyl bromide (30.25 gms.).

The temperature of the reaction flask was brought below 0°C (ice and salt bath). A solution of KOH (14 gms) in methanol was added to the reaction flask over a period of 20 min. The amount of methanol was adjusted to get a homogeneous reaction mixture. t-BuOOH (4.5 gms) was added to the reaction mixture after a period of 5 hrs. Then the reaction mixture was stirred for 10 hrs. The precipitated KBr was filtered off. The filtrate was extracted several times with 20 ml portions of pentane. The combined pentane extract was washed with KOH solution followed by distilled water. The pentane extract was then dried with anhydrous Na₂SO₄ and fractionally distilled under reduced pressure using an 8" column packed with pyrex glass helices. The fraction boiling at 55 -56°C at 75 mm of Hg was 95% pure peroxide (by G.L.C. analysis). This was further purified by gas chromatography and identified as described earlier. Yield 16%.

**1V.**

**Preparation of 3-hydroperoxy 1-Propene.**

Allyl Bromide (36 gms) was dissolved in methanol (250 ml) in a one litre round bottom flask. This mixture was stirred by a magnetic stirrer while the flask was cooled to -5°C (ice and salt bath). Hydrogen peroxide (132 gms.) was added to the reaction flask. Potassium hydroxide solution (16.8 gms in 33.6 gms of water) was added to the stirred solution in the flask within a period of 45 min. Stirring was continued for a period of 12 hrs while
the temperature was allowed to rise from -5°C to room temperature. 

Aliquot of reaction mixture was withdrawn several times to examine for -OOH peak by n.m.r. as the reaction was in progress. Finally the reaction mixture was transferred to a separatory funnel and was extracted with two 50 ml portions of pentane (to remove most of the allyl alcohol and allyl bromide.) The hydroperoxide is much less soluble in pentane. The reaction mixture was then diluted with 250 ml of water and extracted several times with 100 ml portions of peroxide free ether. The combined ether extract was then dried over anhydrous sodium sulphate and distilled at 15 mm pressure at 0°C (ice bath). This distillation removed most of the ether and some methanol. The residual liquid was diluted three times with distilled water and again extracted with two 10 ml portions of peroxide free ether. The dried ether extract showed the presence of hydrogen peroxide and hydroperoxide (by G.L.C. analysis). The column used was 6' 10 % silicone D.C. 200, C.T. 30°C, flow rate 45 ml/min. R.T. of ether 5 min. R.T. of 3-hydroperoxy 1-propene 30.5 min. The hydroperoxide was purified by G.L.C. using the above conditions. \( n_D^{20} 1.402 \) (reported 1.400 \(^{(39)}\)). The hydroperoxide was further identified by n.m.r. and i.r. analyses. Yield 18%.

Attempts to prepare the hydroperoxide by the oxidation of allyl Magnesium bromide were unsuccessful. \(^{(42)}\)

N.M.R. Analysis of hydroperoxide.

In (CD\(_3\))\(_2\)CO the peaks were at 4.5 \(\delta\) (multiplet for CH\(_2\)-O-O), 5.4 \(\delta\)(multiplet for CH\(_2\)=),
$6\delta$ (multiplet for $\text{CH}=\text{CH}$) and at $11\delta$ (sharp singlet for $-\text{OOH}$). A minor impurity gave a single peak at $1.75\delta$.

**I.R. analysis of the hydroperoxide**

Liquid film of the hydroperoxide showed the following major peaks; (in cm$^{-1}$) 3000-3500 ($\text{OH}$ stretching), 2500-3000 ($\text{CH}$ stretching), 1650 ($\text{C}=\text{C}$ stretching) and 1400-1300.

**Purity of hydroperoxide.**

An aliquot sample of the peroxide was treated with 1 gm of NaI and 20 ml of a mixture of acetic acid/isopropanol (1:10) and titrated against 0.1N sodium thiosulfate following the standard procedure. (43) Titrations gave a consistent value of purity, 97%.

**G.L.C. analysis** (6', 10% silicon D.C. 200, C.T. 80, Flow rate 60 ml/min., R.T. of peroxide 2.5 min.) of the hydroperoxide confirmed above value of purity.

**V.**

**Di-t-butylperoxyoxalate.**

Di-t-butyl peroxyoxalate was prepared by following the method of Bartlett (44). This was crystallised from pentane. Yield 31%.

**VI.**

**Preparation of allyl benzyl ether.**

Metallic sodium (6 gm.) was dissolved in freshly distilled allyl alcohol (50 ml) in a round bottom flask. Benzyl chloride (20 gm.) was added over a period of 15 min. The reaction mixture was stirred and gently refluxed
for 3 hrs. The precipitated NaCl was filtered off. Half of the reaction mixture was distilled under atmospheric pressure. At 130° the residual liquid in the flask solidified to an yellow mass (polymerised?). The other half of the reaction mixture was diluted with an equal amount of water and extracted with two 50 ml portions of ether. The combined ether extract was dried over anhydrous MgSO₄ and fractionally distilled in vacuo. The fraction collected at 75° at 20 mm. Hg. was pure allyl benzyl ether. (nmr. analysis.) Yield 30%.

In CDCl₃ the peaks were at 4.0 δ(CH₂ multiplet), 4.5 δ(CH₂ singlet), 5.6 δ(CH=CH multiplet) and 7.4 δ(C₆H₅ singlet).

VII.

**Preparation of 4-phenyl 1-butene** (45)

Allyl bromide (60.5 gm.) was converted to allyl magnesium bromide by following the standard method. The grignard reagent in ether was forced through a U-tube into another reaction flask by increasing the nitrogen pressure. A solution of benzyl chloride (45 gm.) in ether was gradually added to the ethereal solution of the grignard reagent, while the reaction mixture was stirred thoroughly. Stirring was continued for another hour. The reaction mixture was then poured onto crushed ice and hydrolysed with a saturated solution of ammonium sulphate. The organic layer was separated, dried and fractionally distilled. Pure 4-phenyl-1-butene distilled between 180-181°. It was then identified by nmr analysis. Yield 38%.

In CDCl₃ the peaks were at 2-3 δ(CH₂CH₂.
multplet), 4.5-6.5 $\delta$ (CH$_2$CH multiplet) and 7.25 $\delta$ (C$_6$H$_5$ singlet).

VIII.

Preparation of 1,2-epoxy-4-phenyl butane (47)

4-Phenyl-1-butene (13.2 gm.) was dissolved in chloroform (700 ml) in a one litre flask which was then cooled in an ice bath. m.Chloro perbenzoic acid (18 gm) was dissolved in the chloroform solution. The reaction mixture was kept in ice for 24 hrs with occasional shaking during the first hour. At the end of the reaction, excess peracid was detected by the addition of a little reaction mixture to acidified KI solution. (I$_2$ was liberated) The chloroform solution was washed successively with 10% NaOH and distilled water and dried over MgSO$_4$. Most of the chloroform was removed under slight vacuum and the residual liquid was fractionally distilled under reduced pressure. Pure epoxide boiled between 126-127°C at 20 mm.Hg. It was identified by nmr. analysis. Yield 33%.

In CDCl$_3$ the peaks were at 2 $\delta$ (CH$_2$ multiplet), 2.5-3.5 $\delta$ (5H multiplet), and 7.5 $\delta$ (C$_6$H$_5$ singlet).

Kinetic Studies in Toluene.

A standard solution of the peroxide (allyl t-butyl peroxide or 3-hydroperoxy-l-propene) in toluene was placed in a pyrex glass vial with 12 or 16 side ampoules.

*In some of the decompositions the solvent was 1M solution of $\alpha$-methyl styrene in toluene.
The solution was then degassed and sealed off from the vacuum line. The frozen solution in the pig was warmed to room temperature and brought to individual ampoules which were then sealed and cooled in ice water.

The ampoules were then placed in batches of six or eight in a constant temperature silicone oil bath (±0.1°C) and removed at definite time intervals and quenched by immersing in ice cold water. The unreacted allyl t-butyl peroxide was estimated by G.L.C. analysis (8', 20% diisodecyl phthalate on chromosorb W, C.T. 80°C, Flow rate 40 ml/min., R.T. of peroxide 4.8 min., R.T. of toluene 7 min.). The solvent was used as the internal standard. Under the above conditions the peroxide was quite stable to G.L.C. analysis.

Unreacted 3-hydroperoxy-1-propene was also analysed by G.L.C., using a 6', 10% silicone D.C. 200 on gas chrom. Z. (C.T. 80°C, Flow rate 60 ml/min., R.T. of hydroperoxide 2.5 min., R.T. of toluene 4.5 min.). Toluene peak was used as the internal standard. The hydroperoxide was found to be stable towards G.L.C. analysis under these conditions.

**t-Butoxy radical attack on allyl t-butyl peroxide.**

Di-t-butyl peroxyxalate (0.3884 gm) was dissolved in 5 ml of 0.166M solution of the peroxide in toluene (to get 0.332M solution of DBPO). This solution was degassed and sealed in a pyrex tube and the tube was heated
for two hours at 60°. Unreacted peroxide was determined by
G.L.C. analysis. (8', 20% diisodecyl phthalate, C.T. 80°, Flow
rate 40 ml/min., R.T. of peroxide 4.6 min.)

t-BuOH was quantitatively analysed and
other products were qualitatively analysed on 6',20% carbowax
column. (C.T. programmed 50-170°, Flow rate 40 ml/min., R.T. of
acetone 2 min., t-BuOH 2.5 min., bibenzyl 25 min.) The stability of
acrolein under the decomposition conditions was checked.

Stability of acrolein under the conditions of thermal
decomposition of **allyl-t-butyl peroxide**

A solution of 0.2M acrolein was prepa-
red in a solution of 0.1M allyl tert- butyl peroxide in
toluene. This solution was degassed and sealed in a pyrex
tube and heated for ten half lives of the peroxide at 150°.
The solution was then analysed for any remaining acrolein
by G.L.C. (20% carbowax, C.T. 30°, Flow rate 40 ml/min.,
R.T. of acrolein 11 min.)

Stability of allyl benzyl ether under the conditions of
decomposition of **3-hydroperoxy-l-propene**.

A small quantity of allyl benzyl ether
was added to 5 ml of a 0.15M solution of the hydroperoxide.
The original concentration of the ether was determined by
G.L.C. analysis. (20% carbowax, C.T. 170°, Flow rate 40 ml/
min., R.T. of ether 7 min.) The above solution (2 ml)
was then degassed, sealed and heated for ten half lives of
the hydroperoxide at 185°. Any remaining allyl benzyl ether was analysed by G.L.C.

Product Studies.

(a) Allyl t- butyl peroxide in toluene.

5 ml of a 0.2M peroxide solution (with and without α-Methyl styrene) was placed in a pyrex glass bulb equipped with a break seal bulb. This solution was frozen in liquid Nitrogen and degassed on a vacuum line and cut off from the line by means of a flame torch. The solution was then decomposed by immersing and heating in an oil bath at 150° for ten half lives of the peroxide. The bulb was then connected to the vacuum line and the solution was frozen with liquid Nitrogen. The break seal bulb was opened to a Toepler pump. The gases were transferred to a segment of the vacuum line (volume of which was previously determined). The total pressure of the product gases was noted. 10 ml of this gas was injected into the gas chromatograph through a loop connected from the vacuum line to the chromatograph. Calibrations were done before for each of the gases analysed. Molecular sieve 5A and porapak Q columns were used in analysing the gases. (C.T. 55°, Flow rate 40 ml/min., R.T. of CO 16 min., R.T. of CH₄ 8 min.)

The solution was analysed by G.L.C. using internal standards. Acetone, t-BuOH and allyl alcohol were analysed on a 8' 20% di-isodecyl phthalate column by programming the temperature from 75 - 95°. (Flow rate 60 ml/min. R.T. of acetone 147 sec. R.T. of t-BuOH
27

215 sec, R.T. of allyl alcohol 351 sec. ) Bibenzyl and 4-phenyl-1,2-epoxy butane were analysed on a 6' 10% silicone D.C. 200 column. ( C.T. 160°, Flow rate 40 ml/min., R.T. of epoxide 7.5 min., R.T. of bibenzyl 22 min. ) G.C. mass spectral analyses and retention times from G.L.C. were used to identify the products. (b) 3-hydroperoxy-1-propene in toluene.

4 ml of a 0.15M solution of the hydroperoxide in toluene was heated for ten half lives at 185° by following the method described earlier. Gases were analysed by the same method and conditions as that for allyl-t-butyl peroxide.

Six of the nine peaks which appeared on the gas chromatogram of the decomposed solution were identified by G.C. mass spectra and retention times. The concentrations of the others were too small to be identified by G.C. mass technique. Compounds which appeared before toluene peak in the chromatogram were analysed on a 10% ethofat column. ( C.T. 70°, Flow rate 40 ml/min., R.T. of 1,5-hexadiene 2.3 min., R.T. of allyl alcohol 9 min. ) Products which appeared after the toluene peak were analysed on a 20% carbowax column. ( C.T. 170°, Flow rate 40 ml/min., Retention time of 4-phenyl-1-butene 3.6 min., R.T. of benzaldehyde 6.8 min., R.T. of the epoxide 20 min., and R.T. of benzyl alcohol 24 min. ) Internal standards were used in all quantitative work.

Water was not quantitatively analysed in this work; but drops of water were detected in the
decomposed solutions.

In another experiment 4 ml of a 0.15M solution of hydroperoxide in toluene were decomposed to the extent of 22% at 185°. The unreacted hydroperoxide was reduced by triphenyl phosphine (recrystallised from ethanol) to allyl alcohol. The products were qualitatively analysed. (using columns and conditions described earlier)

2 ml of a decomposed hydroperoxide solution was extracted with 5 ml of a standard (0.016 M) solution of NaOH. The NaOH was then back titrated with standard (0.02M) oxalic acid solution using phenolphthalein as the indicator. The total acids present were thus estimated.

Analysis of Residue.

One ml each of the decomposed solutions of the peroxide and the hydroperoxide was placed in a previously weighed pyrex tube and connected to the vacuum line. All the volatile liquids were removed in vacuo. In both cases the semi solid mass left was accurately weighed. The residues were examined by I.R. analysis. The spectra showed a strong absorption at 1725 cm\(^{-1}\) - 1775 cm\(^{-1}\).

Experimental errors.

G.I.C. analysis is generally reproducible to the extent of 2%, the major error being in taking the data from the chart tracing. Peak areas were taken as the average of those from three injections. In quantitative works internal standards were used. Kinetic runs were done two or more times. The product
analyses were carried out in duplicate.
Results and discussion.

Rates of decomposition of allyl-t-butyl peroxide.

Decompositions of allyl-t-butyl peroxide were carried out in toluene and in 1M solution of \( \alpha \)-methyl styrene in toluene over a temperature range of 130-160°C. Decompositions in toluene were carried out with 0.05-0.2M solutions of the peroxide and those in 1M \( \alpha \)-methyl styrene in toluene were carried out with 0.1M solutions of the peroxide. The reaction was followed by monitoring the disappearance of the peroxide by G.L.C. analysis. The decompositions in the above solvents were first order up to the 78% decomposition examined. (Figure 1&2). First order rate constants were independent of initial concentrations, indicating this as the true order of decomposition. The results of these kinetic measurements are given in tables 2 & 3. The logarithm of rate constants were plotted against 1/T and the activation energies \( (E_a) \) were calculated from the slope of the straight line plots. \( E_a \) for the decomposition of allyl-t-butyl peroxide in toluene was found to be 32.8 K.cals/mol and that for the decomposition in 1M \( \alpha \)-methyl styrene in toluene was found to be 36.2 K.cals/mol (Figures 3&4). The log A factors were calculated from the equation

\[
\log A = \log k + \frac{E_a}{2.303 RT}
\]

Log A factor for the decomposition in toluene was 13.65 and
FIRST ORDER PLOTS FOR THE DECOMPOSITION
OF 0.1M ALLYL t-BUTYL PEROXIDE AT 130°

FIGURE 1

IN TOLUENE

--- IN 1M α-METHYL STYRENE

IN TOLUENE.
FIGURE 2

FIRST ORDER PLOTS FOR THE DECOMPOSITION
OF 0.1M ALLYL t-BUTYL PEROXIDE AT 140°

- IN TOLUENE.
- -- IN 1M 1-METHYL STYRENE IN TOLUENE.
FIGURE 3
Arrhenius plots for the decomposition of allyl 1-butyl peroxide in 1M α-methyl styrene in toluene.
FIGURE 4

ARRHENIUS PLOTS FOR THE DECOMPOSITION OF ALLYL E-BUTYL PEROXIDE IN TOLUENE.
### Table 2:
**Rates of Decomposition of Allyl-\(\beta\)-butyl Peroxide in Toluene**

<table>
<thead>
<tr>
<th>Temperature (\degree C)</th>
<th>Concentration</th>
<th>% of Peroxide Decomposed</th>
<th>Rate Constant (k_1 \times 10^5) sec(^{-1})</th>
<th>Correlation Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>130</td>
<td>0.1 M</td>
<td>63</td>
<td>6.61</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>0.2 M</td>
<td>57</td>
<td>6.90</td>
<td>0.997</td>
</tr>
<tr>
<td></td>
<td>0.05 M</td>
<td>55</td>
<td>6.58</td>
<td>0.998</td>
</tr>
<tr>
<td>140</td>
<td>0.1 M</td>
<td>65</td>
<td>19.19</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>0.2 M</td>
<td>66</td>
<td>20.04</td>
<td>0.998</td>
</tr>
<tr>
<td>150</td>
<td>0.1 M</td>
<td>65</td>
<td>49.35</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>0.2 M</td>
<td>69</td>
<td>48.25</td>
<td>0.999</td>
</tr>
<tr>
<td>160</td>
<td>0.1 M</td>
<td>75</td>
<td>115.20</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>0.2 M</td>
<td>69</td>
<td>121.50</td>
<td>0.999</td>
</tr>
</tbody>
</table>
TABLE 3
RATES OF DECOMPOSITION OF ALLYL t-BUTYL PEROXIDE IN 1.0M α-METHYL STYRENE IN TOLUENE.

<table>
<thead>
<tr>
<th>TEMPERATURE °C</th>
<th>CONCENTRATION</th>
<th>% OF PEROXIDE DECOMPOSED</th>
<th>RATE CONSTANT $k_1 \times 10^5$ sec$^{-1}$</th>
<th>CORRELATION COEFFICIENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>130</td>
<td>0.1M</td>
<td>63</td>
<td>5.76</td>
<td>0.999</td>
</tr>
<tr>
<td>140</td>
<td>0.1M</td>
<td>61</td>
<td>17.85</td>
<td>0.998</td>
</tr>
<tr>
<td>150</td>
<td>0.1M</td>
<td>62</td>
<td>48.00</td>
<td>0.998</td>
</tr>
<tr>
<td>160</td>
<td>0.1M</td>
<td>78</td>
<td>127.00</td>
<td>0.998</td>
</tr>
</tbody>
</table>
for decomposition in 1M α-methyl styrene in toluene was 15.4 (table 4).

Activation energies ranging from 34-38 K.cals/mol have been reported for the decomposition of di-alkyl peroxides. Decomposition of di-t-butyl peroxide shows practically the same activation energy in both vapor phase and solution. For dialkyl peroxides the O-O bond energy is reported to be independent on the nature of the alkyl groups. All these suggest that the thermal decompositions of dialkyl peroxides proceed by unimolecular homolysis with very small or negligible contribution from radical induced decomposition. Most of these conclusions were drawn from an intense study of di-t-butyl peroxide decomposition. However, recent studies have proved the cases of induced decomposition in the thermal decomposition of t-Bu₂O₂. Primary and secondary di-alkyl peroxides are more susceptible to self-induced decomposition. Thus we cannot completely rule out the possibility of induced decomposition having appreciable contribution to the overall decomposition of these peroxides. Unlike the di-tertiary peroxides these contain α-H atoms which can be easily abstracted by radicals.

The peroxide in the present work contains a simple allyl group. The allylic hydrogen can be easily abstracted as the resulting radical would be stabilised by the allyl group resonance.
TABLE 4
ACTIVATION ENERGIES FOR THE DECOMPOSITIONS OF
ALLYL ε-BUTYL PEROXIDE.

<table>
<thead>
<tr>
<th>SOLVENT</th>
<th>TEMPERATURE °C</th>
<th>CONCENTRATION</th>
<th>E_a K. cals/mol</th>
<th>LOG A</th>
<th>CORRELATION COEFFICIENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>130-160</td>
<td>0.1 M</td>
<td>32.5</td>
<td>13.47</td>
<td>0.999</td>
</tr>
<tr>
<td>Toluene</td>
<td>130-160</td>
<td>0.2 M</td>
<td>33.2</td>
<td>13.84</td>
<td>0.999</td>
</tr>
<tr>
<td>1.0 M α-Methyl styrene in</td>
<td>130-160</td>
<td>0.1 M</td>
<td>36.2</td>
<td>15.39</td>
<td>0.999</td>
</tr>
<tr>
<td>Toluene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Moreover, another feature of this peroxide is the presence of a double bond to which radicals can be easily added. Both of these phenomena may lead to radical induced decomposition of the peroxide

\[
R-O-O-CH_2-CH=CH_2 + RO. \longrightarrow ROO-CH-CH=CH_2 \\
\text{ROO-\textbf{CH} =CH-CH}_2^{\cdot}
\]

Thus one would expect a higher contribution from radical induced reaction to the overall decomposition of allyl-t-butyl peroxide.

The kinetic order of the induced part of the reaction depends on the source of the radical causing induced decomposition and the nature of the termination step.

\[
(R_1R_2CH)_2O_2 \xrightarrow{k_i} 2R_1R_2CHO. \quad (1)
\]

\[
(R_1R_2CH)_2O_2 + R_1R_2CHO. \xrightarrow{k_p} R_1R_2^{\cdot}O-O-CHR_1R_2 + R_1R_2CHOH \quad (2)
\]
\[
R_1 R_2 C=O + R_1 R_2 CHO \quad \text{(3)}
\]

\[
R_1 R_2 O - O - CHR + R_1 R_2 CHO \quad \xrightarrow{k} \text{non radical products.} \quad \text{(4)}
\]

\[
2 R_1 R_2 CHO \quad \xrightarrow{k'} \text{non radical products.} \quad \text{(5)}
\]

If equation (5) above is the main termination step, at steady state it is reasonable to assume that

\[
\text{Rate of initiation} = \text{Rate of termination.}
\]

\[
2 k_i [P] = 2 k_t' [RO]^2
\]

\[
[P] = \left(\frac{R_1 R_2 CH}{2}\right)^2 \quad [RO] = [R_1 R_2 CHO]
\]

\[
\therefore [RO] = \left(\frac{k_i}{k_t}\right)^{1/2} [P]^{1/2}
\]

\[
-\frac{d[P]}{dt} = k_i [P] + k_p [P] [RO]
\]

\[
= k_i [P] + k_p \left(\frac{k_i}{k_t}\right)^{1/2} [P]^{3/2}
\]

On the other hand with equation (4) as the main termination step at steady state
\[
\frac{d[R_O]}{dt} = 2 k_1 [P] - k_p [R_O] [P] - k_t [P-H] + k [P-H] = 0 \quad (a)
\]

\[
[P-H] = \frac{R_1 R_2 C-O-O-CHR_1 R_2}{k}
\]

\[
\frac{d[P-H]}{dt} = k_p [R_O] [P] - k [P-H] - k_t [R_O] [P-H] = 0 \quad (b)
\]

From equation (b) above,

\[
[P-H] = \frac{k_p [R_O] [P]}{k + k_t [R_O]}
\]

Substituting for \([P-H]\) in equation (a) and solving the quadratic equation for \([R_O]\)

\[
[R_O] = \frac{k_1}{2k_p} + \left[\left(\frac{k_1}{2k_p}\right)^2 + \frac{k_1 k}{k_p k_t}\right]^{\frac{1}{2}}
\]

If \(k_p\) is much larger than \(k_1\), then

\[
[R_O] = \left(\frac{k_1 k}{k_p k_t}\right)^{\frac{1}{2}}
\]

The overall rate of decomposition of the peroxide will then be

\[
- \frac{d[P]}{dt} = 2 k_1 [P] + k_p [P][R_O]
\]

\[
= 2 k_1 [P] + k_p \left(\frac{k_1 k}{k_p k_t}\right)^{\frac{1}{2}} [P]
\]

\[
= 2 k_1 [P] \left[1 + \left(\frac{k_p k}{4 k_1 k_t}\right)^{\frac{1}{2}}\right]
\]
If $k_i$ and $k_t$ are small as compared to $k_p$ and $k$ the second term in the bracket will be much larger than unity. Then

$$\frac{-d[P]}{dt} = \left(\frac{k_i k_p}{k_t}\right)^{\frac{1}{2}} [P]$$

Thus the overall decomposition would be first order in peroxide

$$K_{overall} = \left(\frac{A_i A_p}{A_t}\right)^{\frac{1}{2}} e^{-\frac{E_{ai}}{2} + \frac{E_{ap}}{2} + \frac{E_a}{2} + \frac{E_{at}}{2}}$$

$$E_{a overall} = E_{ai}/2 + E_{ap}/2 + E_a/2 - E_{at}/2$$

$E_{ai} = 36$ K.cals/mol for dialkyl peroxides (49)

$E_{ap} = 7.5$ K.cals/mol (51)

$E_a = 24$ K.cals/mol from the similar free radical reactions of ether. (48)

$E_{at} = 0$ for radical combination is zero. (52)

$$E_{a overall} = \frac{36}{2} + \frac{24}{2} + \frac{7.5}{2} = 33.75$$ K.cals/mol
The experimental value of activation energy for the overall decomposition of allyl tertiary butyl peroxide is very close to the calculated value.

\[ A_{\text{overall}} = \left( \frac{A_p A_i A}{A_t} \right)^{1/3} \]

(51) \hspace{1cm} (49) \hspace{1cm} (48) \hspace{1cm} (52)

\[ A_p = 10^8 \quad A_i = 10^{16} \quad A = 10^{13} \quad A_t = 10^0 \]

A overall value of \((10^{13})\) is in good agreement with the experimentally determined A factor.

When the contribution from the induced decomposition is small as compared to the unimolecular decomposition, deviation from the first order kinetics would be small irrespective of the nature of the termination (eqn. (4) or eqn. (5)). But a change in the initial concentration of the peroxide should indicate the true order of the reaction. If equation (5) is the chain termination step, an increase in the initial concentration of the peroxide at a particular temperature would increase the first order rate constant.

Varying contributions from equations (1) and (3) would cause variation in the values of \(E_a\) and \(A\).

Pryor and co-workers have suggested that, in the peroxide initiated radical polymerisation of styrene, chain transfer \(C_{tr} = k_a/k_p\) occurs by hydrogen abstraction and not by \(S_H\) displacement on the O-O bond of the peroxide by polystyryl radicals. (50)
Primary, secondary & tertiary peroxides tested had about the same chain transfer constant. But thermal decomposition of secondary Bu₂O₂ was found to be much faster and produced hydrogen by a concerted reaction. Allyl-t-butyl peroxide cannot form molecular hydrogen in the solvent cage as one of the alkyl group is tertiary. Radical induced decomposition has been suggested to explain the much faster rate of decomposition of secondary Bu₂O₂.

The relatively low value of the activation energy, 32.8 K. cals/mol observed for the decomposition of allyl-O₂-t-Bu appears to be due to the contribution of induced decomposition to the overall decomposition of the peroxide. This seems to be reasonable as the peroxide is more susceptible to radical attack than other primary or secondary peroxides due to the presence of a neighboring double bond. Addition of solvent radicals or other radicals to this double bond may induce a chain. The first order rate constant of the decomposition is practically unaffected by doubling the initial concentration of the peroxide.
This obviously indicates the cross termination of the radicals resulting in an overall true first order kinetics. The correlation coefficient 0.999 of the first order plots for the decompositions of the peroxide is a good indication of this.

α-Methyl styrene was used as a radical trap in order to test its effect on rates of decomposition of allyl-t-butyl peroxide in toluene. Such radical traps in solution trap the radicals produced by the unimolecular decomposition of the peroxide (or the radical produced by the H-abstraction of the solvent molecules) thereby preventing radical induced decomposition of the peroxide. Radicals add to the double bond of α-methyl styrene (on the side chain). Rates of decomposition of 0.1M allyl-t-butyl peroxide in 1M α-methyl styrene were measured at 130-160°C (see table 3). The rate of decomposition of peroxide was lowered at 130°C when the decomposition was carried out in 1M α-methyl styrene. The rates of decomposition followed first order kinetics with an activation energy of 36.2 K. cals/mol and a log A factor of 15.39. Lowering of rates of decomposition in presence of a radical trap is an indication of radical decomposition. An Ea of 36.2 K. cals/mol and log A of 15.39 are in the usual range for the unimolecular decomposition of dialkyl peroxides. It appears that radical induced decomposition, although not major, contributes to the overall decomposition of allyl-t-butyl peroxide.
Nature of radical attack on allyl-t-butyl peroxide

Allyl-t-butyl peroxide was subjected to t-BuO• radical attack at 60° by heating a 0.166M solution of the peroxide in 0.332M solution of di-t-butyl peroxy oxalate (DBPO) in toluene for two hours. The percentage of decomposed peroxide was determined by G.L.C. analysis. t-Butyl alcohol was analysed quantitatively and other products were analysed qualitatively by G.L.C. analysis (see table 5).

DBPO is reported to decompose at 60° with a half life of 6.8 minutes (44) and it is a good source of t-BuO• radicals.

\[ \text{t-BuO} - \text{O} - \text{C} = \text{O} - \text{t-Bu} \rightarrow 2 \text{t-BuO} + 2 \text{CO}_2 \]

The t-BuO• radicals thus produced in the solvent cage have two choices; either to recombine to form t-Bu₂O₂ which is stable at 60° or abstract hydrogen from toluene to produce benzyl radicals outside the cage. The cage combination of t-BuO• radicals has been reported to be hindered by the presence of two CO₂ molecules in between the radicals in the solvent cage.

\[ \text{t-BuO} . \text{CO}_2 \text{CO}_2 . \text{O} \text{Bu-t} . \]
TABLE - 5

PRODUCTS FROM DBPO INDUCED DECOMPOSITION OF ALLYL t-BUTYL PEROXIDE AT 60°

<table>
<thead>
<tr>
<th>Concentration of Peroxide</th>
<th>Concentration of DBPO</th>
<th>% of Peroxide Decomposed</th>
<th>Acetone</th>
<th>t-BuOH</th>
<th>BIBENZYL</th>
<th>EPOXIDE</th>
<th>ACROLEIN</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.166M</td>
<td>0.332M</td>
<td>25</td>
<td>+</td>
<td>0.71M</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* 1,2-EPOXY-4-PHENYL BUTANE + = PRESENT − = ABSENT.
The radicals thus produced can attack the peroxide which is quite stable at 60° to O-O bond homolysis.

Heating allyl-t-butyl peroxide with DBPO at 60° for two hours decomposed 25% of the peroxide. The products were acetone, t-butanol and bibenzyl. No 4-phenyl-1,2-epoxy butane was detected. Acrolein was found to be unstable under the conditions of DBPO attack of the peroxide. Quantitative estimation of t-butanol accounted for most of the t-BuO\(^{•}\) radicals produced from DBPO and the decomposed peroxide. (Acetone yield was very small.) Bartlett et al have reported the decomposition of DBPO in toluene where no t-Bu\(_2\)O\(_2\) was formed by cage combination of two t-BuO\(^{•}\).\(^{44}\) The absence of any epoxide in the products suggests that the decomposition of allyl-t-butyl peroxide under these conditions did not proceed via the addition mechanism.

\[
\begin{align*}
\text{CH}_2=\text{CH} - \text{CH}_2-\text{O-O-} & \quad \text{t-Bu} + S. \\
\text{S-CH}_2-\text{CH}_2-\text{O-O-t-Bu} & \\
\downarrow & \\
\text{S-CH}_2-\text{CH}_2-\text{CH}_2 + \text{t-BuO}^•. 
\end{align*}
\]

For the addition of alkyl radicals to carbon carbon double bonds
the ceiling temperatures are not similar for different alkyl radicals. This for benzyl radicals may be low. However, it is clear that the DBPO induced decomposition of allyl-\text{-}t\text{-}butyl peroxide at 60^\circ\text{C} proceeds through an abstraction mechanism.

\[
\begin{align*}
\text{CH}_2 = \text{CH} - \text{O-O-t-Bu} + S. & \quad \rightarrow \\
\text{CH}_2 = \text{CH} - \text{O-t-Bu} + \text{SH} & \quad \rightarrow \\
\text{CH}_2 = \text{CH-CHO} + \text{t-BuO}. &
\end{align*}
\]

Quantitative estimation of bibenzyl would have thrown light on the clear picture of the decomposition, but our work was not extended to this due to lack of time. But one point became clear, that unlike \text{sec-butyl peroxide}, \text{allyl-\text{-}t\text{-}butyl peroxide is subject to radical attack at lower temperatures.}
Products of decomposition of allyl-t-butyl peroxide.

Decompositions were carried out by heating 5 ml. of 0.2M degassed solutions of the peroxide in toluene or 1M α-methyl styrene in toluene for a time equivalent to ten half lives of the peroxide. Gaseous and liquid products were qualitatively analysed by G.L.C.

The products of decomposition of the peroxide in toluene were acetone, t-butanol, allyl alcohol, bibenzyl, 1,2-epoxy-4-phenyl butane, carbon monoxide and methane (see table 6). A semi solid residue was left when the mixture of the products was evaporated on a vacuum line. The products of decomposition of the peroxide in 1M α-methyl styrene were acetone, t-butyl alcohol, allyl alcohol, methane and carbon monoxide (see table 7). No epoxide or bibenzyl was detected in the latter case.

Acrolein was an expected product in the decomposition of the peroxide, but none was detected in G.L.C. analysis. An experiment was conducted to test the stability of added acrolein under the conditions of decomposition of peroxide. A 0.2M solution of acrolein in 0.1M peroxide was heated for ten half lives of the peroxide, at 150°C. G.L.C. analysis proved that none of the added acrolein was present in the product mixture.

For decompositions in toluene the yields of tertiary butanol and acetone were almost quantitative.
Table 6
Products from the Decomposition of Allyl-\(t\)-Butyl Peroxide in Toluene.

<table>
<thead>
<tr>
<th>Product</th>
<th>Mole %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>35</td>
</tr>
<tr>
<td>(t)-Butanol</td>
<td>59</td>
</tr>
<tr>
<td>Allyl alcohol</td>
<td>29</td>
</tr>
<tr>
<td>Bibenzyl</td>
<td>15</td>
</tr>
<tr>
<td>4-Phenyl-(1,2)-epoxy butane</td>
<td>8</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>21</td>
</tr>
<tr>
<td>Methane</td>
<td>25</td>
</tr>
<tr>
<td>Residue*</td>
<td>91 gm/mol.</td>
</tr>
</tbody>
</table>

* After evaporation of the volatile products in vacuum.
Table 7

Products from the decomposition of Allyl-t-butyl peroxide in 1M methyl styrene in toluene.

<table>
<thead>
<tr>
<th>Product</th>
<th>Mole %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>30</td>
</tr>
<tr>
<td>t-Butanol</td>
<td>60</td>
</tr>
<tr>
<td>Allyl alcohol</td>
<td>20</td>
</tr>
<tr>
<td>Methane</td>
<td>21</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>25</td>
</tr>
</tbody>
</table>
The yield of bibenzyl is small. The yield of bibenzyl is a measure of the number of radicals diffusing out of the solvent cage, but in the present case the epoxide, which contains benzyl moiety, should also be taken into account. Thus the percentages of bibenzyl and epoxide show that 38% of the radicals (assuming 2 moles of radicals per mole of peroxide) produced escape the solvent cage. Allyl alcohol is a product of H-abstraction and cannot be formed by the disproportionation of allyloxy radicals with t-butoxy radicals in the cage. Methane is formed by the H-abstraction of methyl radicals resulting from the β-scission of t-butoxy radicals.

\[
\text{t-BuOO-CH}_2\text{-CH} = \text{CH}_2 \rightarrow \text{t-BuO.} + \text{.O-CH}_2\text{-CH} = \text{CH}_2
\]

\[
\text{t-BuO.} \rightarrow \text{Me}_2\text{CO} + \text{Me.}
\]

\[
\text{t-BuO.} \quad \text{(Me.)} + \quad \text{C}_6\text{H}_5\text{CH}_3 \quad \rightarrow \quad \text{C}_6\text{H}_5\text{CH}_2. + \quad \text{t-BuOOCH}_2\text{-CH} = \text{CH}_2 \quad \text{(t-BuOO CH -CH=CH}_2\text{)}
\]

\[
\text{t-BuOH} \quad \text{(MeOH)} \quad \text{(CH}_2\text{-CH - CH}_2\text{OH)}
\]

t-BuO. and allyloxy radicals can disproportionate in the solvent cage.
t-BuO. + CH₂=CH - CH₂O. $\rightarrow$ t-BuOH + CH₂=CH -CHO

The epoxide is obviously a product of induced decomposition and from the yield of the epoxide the induced decomposition by addition mechanism should be at least 8%.

If we assume that t-butanol is produced by the above route and cage disproportionation, it appears that about 50% of t-BuO. radicals take part in the disproportionation reaction in the cage.

The mechanism of carbon monoxide formation is not quite clear. Aldehydes are easily attacked by radicals to form carbon monoxide gas.

R-CHO + S. $\rightarrow$ R-C-O + SH $\rightarrow$ R. + CO + SH

Application of this mode of reaction to the present work should produce reactive vinyl radicals in solution which should either abstract hydrogen from the solvent or take
part in other radical reactions. But the decomposition product did not show the presence of ethylene gas or other vinyl group containing organic molecules. Addition of vinyl radicals to toluene can result in methyl styrene which might polymerise under the reaction conditions. Another possibility is the formation of carbon monoxide from the acrolein polymer by radical reactions. One expected product, allyl benzyl ether was shown to be unstable at these decomposition temperatures.

For simplicity, if we take the rate of decomposition of the peroxide in toluene as the sum of the rate of unimolecular homolysis and rate of induced decomposition and that in 1M α-methyl styrene as the rate of unimolecular homolysis, the percentage of induced decomposition at 130º would be 12.5% (tables 2&3). At least 8% of this should be through addition mechanism. There is uncertainty about the remaining 4.5% which might be partly due to addition of other radicals or through the abstraction mechanism. Therefore it appears that induced decomposition via addition of radicals predominates in the decomposition of allyl-t-butyl peroxide.

Rates of decomposition of 3-hydroperoxy-1-propene in toluene.

Rates of decomposition of 3-hydroperoxy-1-propene (allyl hydroperoxide) were measured by following the change in concentration of the hydroperoxide by G.L.C.
analysis. The hydroperoxide was found to decompose on some polar columns such as di-isodecylphthalate and carbowax.

Kinetic studies were done over a concentration range of 0.05M-0.15M solutions in toluene at 165-185°C (see table 8). Decompositions were carried out to the extent of 90%. I tried to fit the analytical data into the standard rate expressions for integral and fractional orders of reaction. None of them gave straight lines but resulted in smooth curves. Therefore I tried to calculate the initial rates by drawing straight lines with as many initial points as possible. First order, second order and half order rate constants thus calculated were highly dependent on initial concentration of the hydroperoxide. But the three halves order rate constant was practically the same for different initial concentrations at a particular temperature (Figure 5). These values are given in table 8. Thus it appears the hydroperoxide decomposes initially by following three halves order kinetics. The rate constants and the correlation coefficients are shown in table 8. The plot of log k against 1/T was linear with a correlation coefficient of 0.998 (Figure 6). The activation energy for the decomposition was 30.2 K.cals/mol with a very low log A factor of 10.6 (see table 9).

Three halves order kinetics shown by the decomposition is a good indication of the fact that
FIGURE - 5

$3/2$ ORDER PLOT FOR THE DECOMPOSITION OF 0.05M ALLYL HYDROPEROXIDE IN TOLUENE at 185.5°
FIGURE 6

ARRHENIUS PLOTS FOR THE DECOMPOSITION OF ALLYL HYDROPEROXIDE IN TOLUENE.
<table>
<thead>
<tr>
<th>TEMPERATURE °C</th>
<th>CONCENTRATION</th>
<th>% OF HYDROPEROXYDECOMPOSED</th>
<th>RATE CONSTANT $k \times 10^4$ M$^{-1/2}$ SEC$^{-1}$</th>
<th>CORRELATION COEFFICIENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>165</td>
<td>0.1 M</td>
<td>80</td>
<td>0.48</td>
<td>0.998</td>
</tr>
<tr>
<td>176.5</td>
<td>0.05 M</td>
<td>83</td>
<td>1.32</td>
<td>0.993</td>
</tr>
<tr>
<td></td>
<td>0.1 M</td>
<td>91</td>
<td>1.35</td>
<td>0.994</td>
</tr>
<tr>
<td></td>
<td>0.15 M</td>
<td>86</td>
<td>1.32</td>
<td>0.985</td>
</tr>
<tr>
<td>185.5</td>
<td>0.1 M</td>
<td>92</td>
<td>2.30</td>
<td>0.996</td>
</tr>
</tbody>
</table>
Table 9

Activation energy for the decomposition of 3-hydroperoxy-1-propene in toluene

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Concentration (M)</th>
<th>Eₐ (kcal/mol)</th>
<th>Log A</th>
<th>Correlation Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>165 - 1855</td>
<td>0.1M</td>
<td>30.2</td>
<td>10.6</td>
<td>0.998</td>
</tr>
</tbody>
</table>
the hydroperoxide decomposes with much less contribution from unimolecular homolysis and the major contribution is from radical induced chain. Hiatt and Irwin suggested the following mechanism for the decomposition of t-BuOOH in toluene where the induced part of the decomposition was 3/2 order in the hydroperoxide. (18)

\[
\begin{align*}
\text{ROOH} & \rightarrow \text{RO} + \cdot \text{OH} \\
\text{RO} + (\cdot \text{OH}) + \text{C}_6\text{H}_5\text{CH}_3 & \rightarrow \text{ROH} + \text{C}_6\text{H}_5\text{CH}_2\cdot \\
\text{RO} + (\cdot \text{OH}) + \text{ROOH} & \rightarrow \text{ROH} + \text{C}_6\text{H}_5\text{CH}_2\cdot + \text{ROO}.
\end{align*}
\]

\[
2 \text{ROO} \rightarrow 2 \text{RO} + \text{O}_2
\]

\[
\text{C}_6\text{H}_5\text{CH}_2\cdot + \text{ROOH} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{OH} + \text{RO}.
\]

In the case of allylic hydroperoxides the chain character would be extremely complex as they can act both as initiator and transfer agent for ROO. A study of the decomposition of 3-hydroperoxy-2,3-dimethyl-1-butene by Hiatt and Mc Carrick concluded that the induced decomposition occur via addition to the double bond of the hydroperoxide. (37)

\[
\begin{align*}
\text{ROOH} & \stackrel{k_1}{\rightarrow} \text{RO} + \cdot \text{OH}
\end{align*}
\]
RO. (OH) + SH → S. + ROH (HOH)  \text{SH = SOLVENT.}

S. + ROOH \xrightarrow{k_2} S'. (SH + ROO.)

S'. = S-CH₂CMe CMe₂OOH

ROO.' + ROOH \xrightarrow{k_2'} S'.'

S'.' = ROO-CH₂CMe CMe₂OOH

S. + S. (S' or S'') \xrightarrow{k_3} \text{non radical products.}

If \( k_2 = k_2' \) then \( k_3 \) for all terminations is about the same.

Applying steady state approximation to radical concentration
the above mechanism gives the rate expression (37).

\[
-\frac{d \text{ROOH}}{dt} = k_1 [\text{ROOH}] + k_2 \left( \frac{k_1}{k_3} \right)^{1/2} \left[ \text{ROOH} \right]^{3/2}
\]

But the allylic hydroperoxide in
this work is a primary one. This leads to the possibility
of abstraction of the allylic hydrogen atom followed by the
homolysis of the O-O bond.

ROOH → RO. + .OH

RO. (OH) + SH → ROH (HOH) + S. (S. = C₆H₅CH₂)
The above mechanism will lead to three halves order kinetics.

(8) Allyl alcohol, acrolein, oxygen and water would be the major products of the above mechanism.

The activation energy for the decomposition of allyl hydroperoxide seems to be very low. The low activation energy and log A factor may be due to the production of many more radicals than could be accounted for.

**Products of decomposition of 3-hydroperoxy-1-propene.**

Four ml of a 0.15M degassed solution of the hydroperoxide in toluene was heated for a time equivalent to ten half lives of the hydroperoxide at 185°.

Both the gaseous and the solution products were analysed by G.LC. The acids were estimated by back titration method using standard sodium hydroxide solution and oxalic acid solution. The residue was estimated by evaporating off the volatile materials on a vacuum line. The products esti-
mated are shown in table 10. The products were 4-phenyl-1-butene, benzaldehyde, benzyl alcohol, allyl alcohol, 1,2-epoxy-4-phenyl butane, carbon monoxide and acids. Trace of ethylene gas was detected. Acrolein, an expected product of decomposition is shown to be unstable under the decomposition conditions. A minor quantity of 1,5-hexadiene was detected by G.C./M.S. but was too small to be estimated quantitatively. No bi-benzyl was detected in the products. Another gas was detected whose retention time was slightly higher than that of ethylene and was tentatively assigned to propene. This was not estimated quantitatively. Estimation of water was not done; but droplets of water separated in the decomposed solutions of the hydroperoxide. Allyl benzyl ether, another expected product was unstable under the decomposition conditions.

In another experiment four ml of a 0.15M solution of the hydroperoxide in toluene was partially decomposed to the extent of 22%; the undecomposed hydroperoxide was decomposed by triphenyl phosphine to alcohol. The gaseous as well as the liquid products were qualitatively examined (see table 11). Oxygen, allyl alcohol 1,5-hexadiene, 4-phenyl-1-butene and benzaldehyde were present. No bi-benzyl, epoxide, or benzyl alcohol was found in the products.
Table 10

Products from the decomposition of 3-hydroperoxy-1-propene in toluene.

<table>
<thead>
<tr>
<th>Product</th>
<th>Mole%</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Phenyl-1-butene</td>
<td>3</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>8</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>14</td>
</tr>
<tr>
<td>Allyl alcohol</td>
<td>18</td>
</tr>
<tr>
<td>4-Phenyl-1,2-epoxy butane</td>
<td>4</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>14</td>
</tr>
<tr>
<td>Ethylene</td>
<td>(trace)</td>
</tr>
<tr>
<td>Acids</td>
<td>7</td>
</tr>
<tr>
<td>Residue*</td>
<td>33 gm/mol.</td>
</tr>
</tbody>
</table>

* After evaporation of the volatile products in vacuum.
TABLE 11

PRODUCTS FROM THE PARTIAL DECOMPOSITION OF 3-HYDROPEROXY-1-PROPENE

<table>
<thead>
<tr>
<th>[RO₂H]</th>
<th>% RO₂H DECOMPOSED</th>
<th>OXYGEN</th>
<th>ALLYL ALCOHOL</th>
<th>1,5-HEXADIENE</th>
<th>4-PHENYL-1-BUTENE</th>
<th>BENZALDEHYDE</th>
<th>BENZYL ALCOHOL</th>
<th>EPOXIDE</th>
<th>8-BENZYL</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15M</td>
<td>2.2</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

+ = PRESENT  - = ABSENT.
The variety of products and their distribution is indicative of the complex set of reactions going on during the decomposition. The formation of oxygen gas in the partial decomposition of the hydroperoxide may be due to a reaction

\[ 2 \text{ROO} \rightarrow 2 \text{RO} + \text{O}_2 \]

But partial decomposition of the hydroperoxide also shows the presence of 1,5-hexadiene and 4-phenyl-1-butene. These are obviously the products derived by the combination of an allyl radical with another or with a \( \Phi CH_2 \). Propene must be the product of hydrogen abstraction by allyl radicals. Benson has calculated the ceiling temperatures for the reaction (53)

\[ R^* + O_2 \xrightleftharpoons[K_{eq}]{} K_{eq} \xrightarrow{RO_2^*} \]

When \( R^* \) alkyl the ceiling temperatures are quite high. But when the radicals are stabilised by resonance as in the case of allyl radical \( K_{eq} \) for the reaction at 227\(^\circ\) in the vapor phase favours the formation of allyl radicals. Ceiling temperatures (the temperature at which \( (\text{ROO})/(R^*)=1 \)) at an oxygen partial pressure of 1 atm. is 300\(^\circ\) and at 0.001 atm. is 90\(^\circ\) when \( R^* \) allyl. But \( R^*O_2 \) is a very fast bimolecular reaction as compared to competing reactions of \( R^* \) such as H-abstraction or addition to olefins and the decomposi-
tion of ROO at ceiling temperature or higher is expected to be a fast unimolecular reaction compared to H-abstraction. At higher temperatures and fixed oxygen pressures (ROO)_eq \approx (R_c)_eq. It should be noted that for a product turnover it is not necessary to be above the ceiling temperature. The actual course of the reaction is determined by the relative rates of radical reactions and their concentrations. Allyl radical formation in this way is one of the possibilities.

The system under consideration in this work is complex and we consider other possibilities of allyl radical formation.

\[
\begin{align*}
\text{CH}_2\text{CH-CH}_2\text{OOH} + \text{RO} & \rightarrow \text{RO-CH}_2\text{CH-CH}_2\text{OOH} \\
& \downarrow \\
& \text{RO-CH}_2\text{CH}_2\text{CH}_2\text{OOH} \\
& \downarrow \\
& \text{RO-CH-CH}_2\text{CH}_2\text{OOH} \\
& \downarrow \\
& \text{OHC - CH}_2\text{CH}_2\text{OOH} + \text{R}.
\end{align*}
\]

or,

\[
\begin{align*}
\text{CH}_2\text{CH-CH}_2\text{OOH} + \text{RO} & \rightarrow \text{RO-CH}_2\text{CH-CH}_2\text{OOH} \\
& \downarrow \text{O}_2 \\
& \text{RO-CH}_2\text{CH-CH}_2\text{OOH} \\
& \downarrow \text{O}_2 \\
& \text{RO-CH-CH-CH}_2\text{OOH} \\
& \downarrow \\
\text{R} + \text{OHC - CH-OOH} \\
& \text{CHOOH}
\end{align*}
\]
The possibility of allyl radicals derived from allyl benzyl ether by radical attack is ruled out as the ether is quite unstable at these decomposition temperatures. This has been demonstrated as the added allyl benzyl ether decomposed under the decomposition conditions of 0.15M hydroperoxide in toluene at 185°C. Polymerised allyl benzyl ether might account for part of the residue.

Benzyl alcohol and benzaldehyde are products derived from benzyl radical. The comparatively higher yields of these products in the decomposition of allyl hydroperoxide (c.f. 3-hydroperoxy-2,3-dimethyl-1-butene) (37) and the absence of bibenzyl lead to the conclusion that any benzyl radical produced in the decomposition of the hydroperoxide is used up. The oxygen produced in the initial stages of the decomposition reacts with both benzyl and allyl radicals, producing aldehydes and carboxylic acids.

\[
R\text{-CH}_2\cdot + O_2 \rightarrow R\text{CHO} \rightarrow ROO\text{H}
\]

A certain amount of alcohol is produced in the above reactions as it may lead to the formation of alkoxy radicals.

There has been some evidence for the formation of benzyl alcohol by an SH² attack of \(\text{C}_6\text{H}_5\text{CH}_2\) radicals on the O-O bond of t-BuOOH (18). t-BuOOH was decomposed both in toluene and cumene at 181.5°C. The yield of t-butanol and acetone in the former case was approximately
the same (46-47%) whereas the yields of cumyl alcohol and acetophenone were 47% and 8.3% respectively. The yield of benzyl alcohol was almost independent of the initial concentration of t-BuOOH. But it is known that cleavage of cumyloxy radicals occur more readily than that of t-BuO\textsubscript{.} radicals. At 182° cumyl hydroperoxide in toluene gives 1.6 times as much acetophenone as cumyl alcohol. This is reasonable as acetophenone is stabilised by resonance whereas acetone is not. The decomposition of t-BuOOH in toluene gives approximately equal amounts of acetone and t-butanol but in cumene gives 5-6 times as much cumyl alcohol as acetophenone. Obviously most of the cumyl alcohol is not formed from the cleavage of cumyloxy radicals. Coupling of \textbullet{OH} and cumyl radicals can be ruled out due to the low steady state concentration of the latter. The other possibility is the SH\textsuperscript{2} attack by these solvent radicals on the \textbullet{}0-0 bond of the hydroperoxide.

\[
\text{S.} + \text{ROOH} \quad \xrightarrow{\text{SH}} \quad \text{RO.} + \text{SOH}
\]

In the decomposition of allyl hydroperoxide in toluene, 8% of benzaldehyde and 14% of benzyl alcohol are formed. We suggest that part of the benzyl alcohol is formed from the reaction of \text{C}_6\text{H}_5\text{CH}_2. and \text{O}_2 and part of it by the induced decomposition of the hydroperoxide by an SH\textsuperscript{2} attack of the benzyl radicals on
The yield of allyl alcohol is very low (18%). Allyl alcohol is formed in the decomposition by the H-abstraction of allyloxy radicals. Interaction of two allyl peroxy radicals can also produce allyl alcohol as one of the products. The low alcohol yield shows the trend that was observed for 3-hydroperoxy-2,3-dimethyl-1-butene (37). Assuming the same behaviour for allyloxy radicals as in the decomposition of allyl-t-butyl peroxide, 50% of the allyloxy radicals should give rise to 16.5% of allyl alcohol in the final product. Taking into account the mechanism proposed by Hiatt and McCarrick (37) 50% of the allyloxy radicals should correspond to the entire decomposition.

\[
\text{ROO} + \text{CH}_2\text{CH} = \text{CH}_2\text{OOH} \rightarrow \text{ROO-CH}_2\text{CH} = \text{CH}_2\text{OOH} \\
\downarrow \\
\text{RO} + \text{CH}_2\text{CH} = \text{CH}_2\text{OOH}
\]

or,

\[
\text{ROO-CH}_2\text{CH} = \text{CH}_2\text{OOH} \rightarrow \text{ROO-CH}_2\text{CH} = \text{CH}_2 + \text{.OH} \\
\downarrow \\
\text{RO} + \text{OCH}_2\text{CH} = \text{CH}
\]

The formation of other products and the primary nature of allyl hydroperoxide suggest other routes of decomposition.
Although the above mechanism may be operative, it cannot account for the entire decomposition of allyl hydroperoxide.

Another product of interest is 4-phenyl-1,2-epoxy butane. Clearly this epoxide is a product of induced decomposition by addition mechanism

$$\text{C}_6\text{H}_5\text{CH}_2 + \text{CH}==\text{CH}-\text{CH}_2\text{OOH} \rightarrow \text{C}_6\text{H}_5\text{CH}-\text{CH}_2\cdot\text{CH}-\text{CH}_2\text{O-O-H}$$
$$\downarrow$$
$$\text{C}_6\text{H}_5\text{CH}_2\cdot\text{CH}_2\text{O-O-CH}_2 + \cdot\text{OH}$$

Four percent of the decomposition appears to proceed through this path as 4% of the epoxide found in the final product (some epoxide may isomerise to aldehyde).

Carbon monoxide in these decompositions can be formed by various reactions. One possibility is the radical reaction on acrolein (see earlier discussion). The trace of ethylene gas detected is probably derived from the vinyl radicals by H-abstraction.

$$\text{SH} + \text{CH}=\text{CH} \rightarrow \text{CH}=\text{CH}_2 + \text{S}.$$  

Epoxides can isomerise at high temperatures to aldehydes which by radical attack can produce carbon monoxide.

$$\text{CH}=\text{CH}-\text{CH}_2\text{OOH} + \text{ROO}. \rightarrow \text{ROO} - \text{CH}=\text{CH}_2\text{OOH}$$
$$\downarrow$$
$$\text{ROO} + \text{CH}_2\text{O-O-CH}-\text{CH}_2\text{OOH}$$
An attempt was made to study the nature of the residue from the decomposition of the hydroperoxide by I.R. analysis. The only useful information obtained from such spectrum was that it contained carbonyl groups. These might be from the polymerised acrolein.

Thus one can see the variety of reactions and products that is found in allyl hydroperoxide decomposition. The simple allyl hydroperoxide is not much different from the other members of the class. But in this work we could bring out a clear picture of most of the products of decomposition.
Conclusions

Studies on allyl-t-butyl peroxide proved that the major path of induced decomposition in the thermolysis of this peroxide is through the addition of radicals. This supports the assumption made by Hiatt and McCarrick (37) in their study of the thermal decomposition of $3$-hydroperoxy-2,3-dimethyl-1-butene. Allyl-t-butyl peroxide is attacked by free radicals at lower temperatures via abstraction mechanism.

The decomposition of allylic hydroperoxide even in the case of the simplest member of the series is a complex one. The kinetic order of the decomposition is indicative of radical induced chains and the low activation energy and A factor is a good indication of enormous radical production by some path. Chain branching reaction is one possibility. It differs from the tertiary allylic hydroperoxide in many respects. Allyl peroxy radicals would be expected to terminate non-radical products rather easily. Allyl hydroperoxide has allylic hydrogens activated by the O-O bond. This provides an easy pathway of H-abstraction by radicals. SH$_2$ radical attack on allyl hydroperoxide seems to be easy as compared to tertiary hydroperoxide which is sterically more hindered. This is proved by the high yield of benzyl alcohol.

Our present work does not support the idea of 'bimolecular initiation' of the hydroperoxide(33). Of course our work was not extended to olefinic solvents.
and temperatures used were rather high. Further work in this line and low temperature radical attack on the hydroperoxide are suggested. But it supports to a good degree the radical addition mechanism at higher temperatures and the idea of enormous radical production by chain branching mechanisms. Our hydroperoxide could not completely decompose by this pathway as other routes were open for free radical induced decomposition. The low yield of alcohol was similar to the observation by other workers. \(^{(37)}\) Production of allyl radicals in the system is a new observation. Our product analysis is much more comprehensive and more complete than in many of the other studies on allylic hydroperoxides. Finally this work opens ways for studies on this and other allylic peroxides and hydroperoxides.
References:
13. R.R. Hiatt and P.M. Rahimi, Unpublished work.


Appendix.

Peroxide concentration vs time for kinetic runs.

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