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The Decomposition of 2,2-Bis(tert-Butylperoxy)-butane under High Pressure

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ABSTRACT

The thermal decomposition of the bifunctional peroxide 2,2-bis(tert-butylperoxy)butane was investigated in a flow reactor at temperatures of 135 to 212°C and pressures of up to 2000 bar. The concentration of the peroxide in isododecane was varied between 1 and 22% by weight. The rate of decomposition measured was used to determine the energy of activation ($E_A = 151.1 \pm 3$ kJ/mol) and the activation volume ($\Delta v'' = 22.3$ mL/mol). Up to a peroxide concentration of 5% by weight, the decomposition takes place according to a first-order rate equation. Above this concentration, induced decomposition takes effect. Gas chromatographic analysis showed that the liquid decomposition products consisted mainly of acetone and tert-butyl alcohol apart from methyl ethyl ketone, propionic acid methyl ester, acetic acid ethyl ester, tert-butyl methyl ether, and oligomers of the solvent. The gaseous decomposition products consisted of methane and carbon dioxide as well as small quantities of ethane, propane, and ethylene. A theoretical explanation of the mechanism of decomposi-

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tion is postulated which explains the spectrum of these components and its changes as a function of the peroxide concentration, the residence time, the temperature, and the pressure.

INTRODUCTION

Organic peroxides containing two or more O–O groups may provide certain advantages when used as new initiators for the high-pressure polymerization of ethylene and other monomers. The decomposition, under the effect of heat, into several radical fractions is capable of influencing both the rate of polymerization and the specific initiator consumption as well as the structure and the molecular weight of the polymer. The decisive factor in this respect is the number and the type of the radical fractions involved and the way in which they are formed and react [1].

The investigation described here was carried out in order to obtain information on the decomposition mechanism of a commercially available bifunctional peroxide, namely 2,2-bis(tert-butylperoxy)butane. In particular, clarification was sought on the effect of the decomposition reaction of the high pressures and temperatures used in industrial-scale polymerization.

EXPERIMENTAL

2,2-Bis(tert-butylperoxy)butane is a colorless liquid. It is supplied in a concentration of 50% by weight with an aliphatic hydrocarbon phlegmatizer. Its main characteristic data are given in Table 1. For the investigation of the decomposition mechanism, the peroxide was diluted with i-dodecane to concentrations of 22 to 1% by weight.

The measurements were carried out in a flow reactor at pressures of up to 2000 bar at temperatures of 135 to 212°C. The reactor has been described in detail in an earlier publication [3]. It consists of a thermostated tube reactor of 0. 5 mm diameter and 2. 730 mm length into which the peroxide solution is fed continuously by means of a high-pressure diaphragm pump. After leaving the reactor, the reaction mixture is subjected to intensive cooling and returned to normal pressure in a separating vessel where the gaseous and the liquid decomposition products are separated. Following various experiments with liquid chromatography and IR spectroscopy, the decomposition products were analyzed by gas chromatography, using a flame ionization detector (FID) for the liquid phase and a thermal conductivity detector (TCD) for the gas phase. The gas chromatographic data and the operating conditions are detailed in Table 2. The residual peroxide content was determined by iodometry [4].

TABLE 1. Data of the Peroxide Examined (according to Ref. 2)

Temperature for a half-life of 1 min[a]	165°C
Density at 20°C	0.81 g/mL
Viscosity at 20°C	1.7 mPa·s
Refractive index at 20°C	1.416
Flash point	> 40°C
Active oxygen content	minimum 6.55% by weight

[a] 0.1 M in isododecane.

TABLE 2. Data Concerning the Gas Chromatographic Analysis

Apparatus	Varian Aerograph 1440	Varian aerograph 1420
Detector	FID (flame ionization detector)	TCD (thermal conductivity detector)
Column	12' length, 1/8" diameter, 30% silicone rubber GE-SF-96 on Chromosorb W-AW 60-80 mesh	12' length, 1/8" diameter, Porapak Q 100-120 mesh
Injector temperature	100°C	175°C
Column temperature	40-100°C	75°C
Heating rate	20°C/min	Isothermal
Detector temperature	195°C	110°C
Sample loop temperature	-	60°C
Bridge current	-	150 mA
Carrier gas stream	Nitrogen, 68 mL/min	Helium, 32 mL/min
Combustion gas streams	Nitrogen, 32 mL/min; compressed air, 172 mL/min	-

RATE OF DECOMPOSITION

First, the influence of the peroxide concentration of the solution on the rate of decomposition at normal pressure and a temperature of 200°C was investigated. For this purpose the residual peroxide concentration at the flow reactor outlet was measured for different residence times. The rate of decomposition was then determined by differentiation of the concentration/time curves. Figure 1, left-hand side, shows the concentration/time curve plotted as an example of an initial peroxide concentration of 4 wt%.

The rate of reaction r plotted on a logarithmic scale against the logarithm of the actual peroxide concentration c_p gives a straight line (Fig. 1, right-hand side) whose slope, according to the expression

$$\log r = \log k + n \log c_p \tag{1}$$

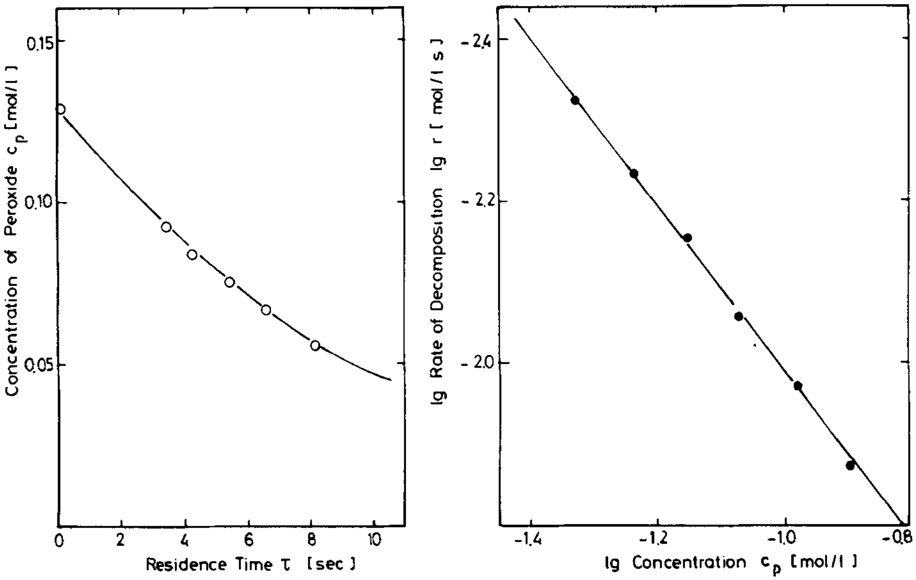


FIG. 1. Results of peroxide decomposition. Temperature: 200°C. Pressure: Ambient. Initial concentration of peroxide: 4.0 wt%. Left: Concentration-time diagram. Right: Plot for the determination of the order of the rate equation.

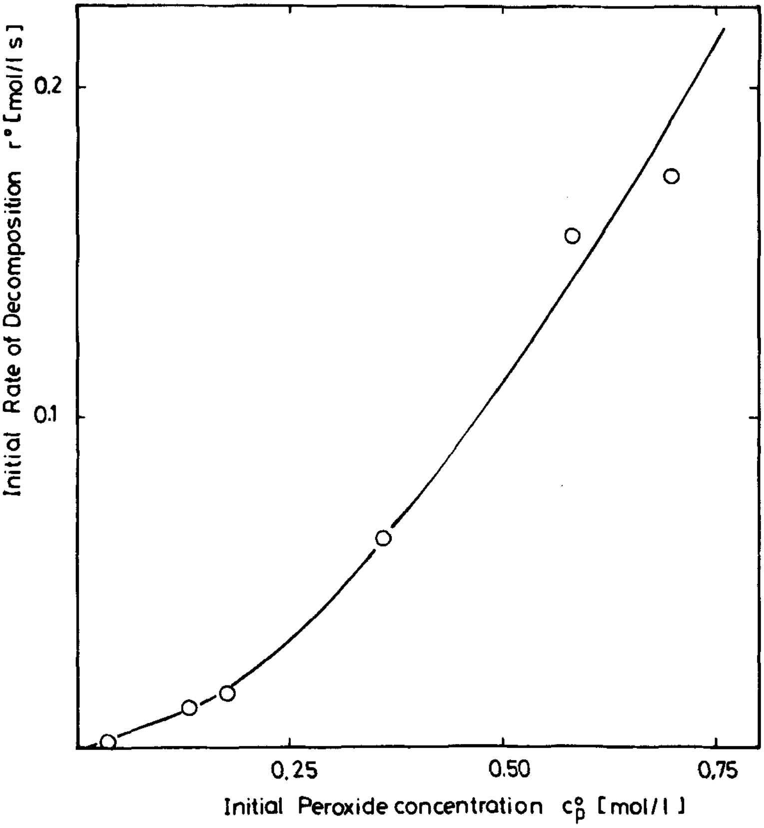


FIG. 2. Initial rate of decomposition. Temperature: 200°C. Pressure: Ambient.

indicates an order of reaction of n = 1. The ordinate intercept can be used to determine the rate constant k and consequently the decomposition half-life $t_{1/2}$ using the expression

$$t_{1/2} = (\ln 2)/k \quad (2)$$

To be able to assess a wider range of concentration, the peroxide concentration of the feed was increased to 22 wt%. As shown in Fig. 2 in which the initial rate of decomposition ($\tau \to 0$) is plotted against the feed peroxide concentration, the decomposition takes place according to a first-order rate equation up to a peroxide concentration of 5 wt%. An induced decomposition takes effect at higher concentrations. In this case the rate of decomposition increases according to the second term of the equation

$$r = kc + k'c^{n'} \qquad (3)$$

this increase being greater than the increase that would be linear due to the concentration.

The initial rate of decomposition r° measured as a function of the peroxide concentration was used to determine the parameters of Eq. (3) as being $k = 0.102$, $k' = 0.225$, and $n' = 1.9$. The correlation between the concentration and the rate of decomposition is greater than indicated in the literature [5, 6] for the induced decomposition of monofunctional peroxides (n' monofunctional = 1 to 1.5).

The influence of the temperature on the rate of decomposition was then determined at normal pressure with a peroxide concentration of 1% by weight with which the possibility of induced decomposition taking place can be discounted. The values measured are plotted in Fig. 3 in the form of an Arrhenius diagram. The gradient of the straight line obtained was used to determine an energy of activation of $E_A = 151.1 + 3$ kJ/mol which is in line with the literature data [7, 8].

To determine the influence of the pressure which provides important information on the decomposition mechanism, measurements were carried at 200°C with a peroxide concentration of 1% by weight. The pressure was increased to 2000 bar. As in the case of the monofunctional peroxides, the half-life decreases considerably with increasing pressure (Fig. 4). However, the increase is much larger. Whereas the half-life increases by a factor of 1.1 to a maximum of 2 when the pressure is increased to 2000 bar during the decomposition of monofunctional peroxides, the half-life of the bifunctional peroxide examined increases by a factor of approximately 3 in the same pressure range.

The rate constant decreases correspondingly with increasing pressure. By plotting the values obtained on a logarithmic scale (Fig. 5), a straight line is obtained, the gradient of which can be used to determine, by using the known expression

$$\left.\frac{\partial \ln k}{\partial p}\right|_T = -\frac{\Delta v^*}{RT} \qquad (4)$$

the volume of activation being $\Delta v^* = 22.3$ mL/mol.

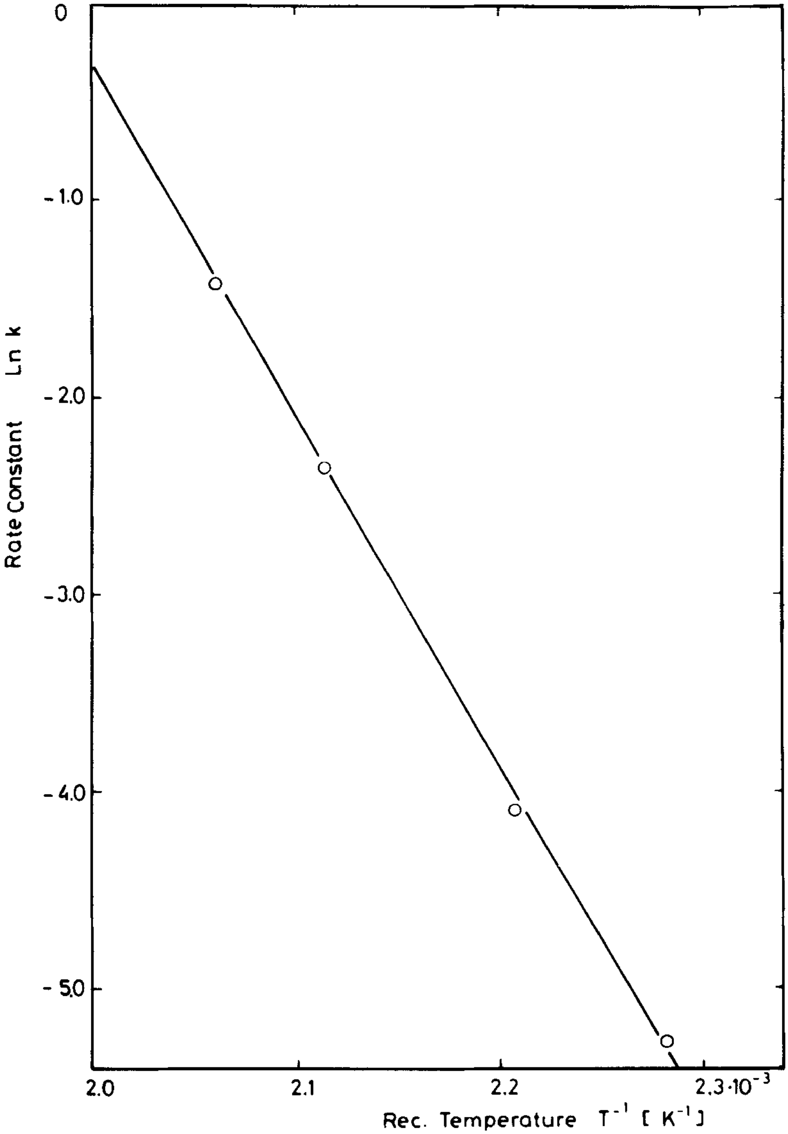


FIG. 3. Rate constant as a function of the temperature. Pressure: Ambient. Concentration of peroxide: 1 wt%.

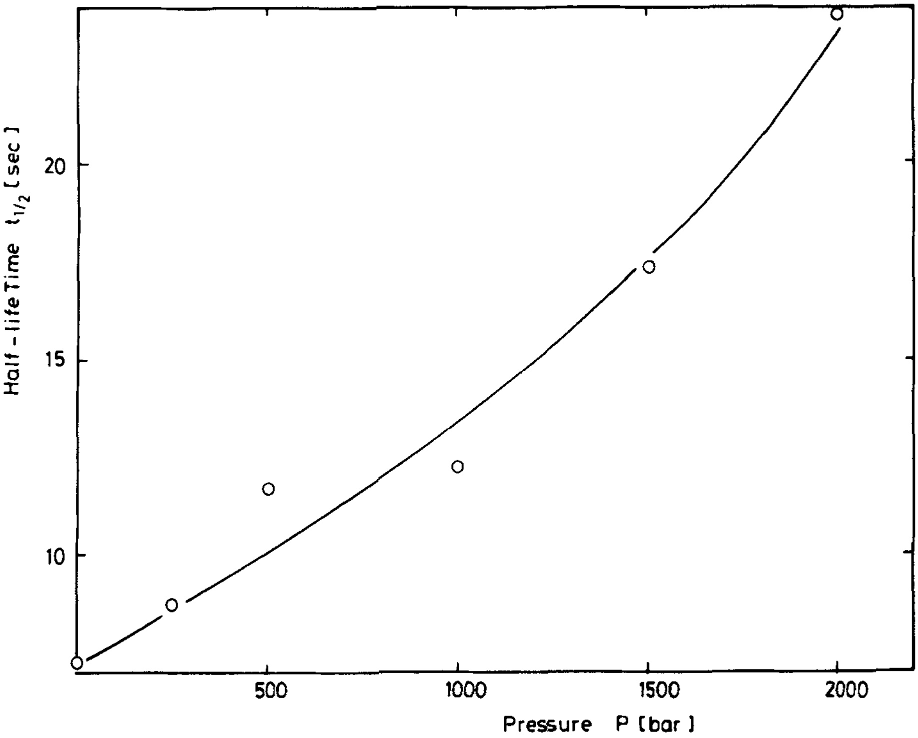


FIG. 4. Influence of the pressure on the half-life. Temperature: 200°C. Concentration of peroxide: 1 wt%.

DECOMPOSITION PRODUCTS

The products obtained in appreciable quantities from the decomposition of 2,2-bis(tert-butylperoxy)butane are listed in Table 3. The main component of the gaseous decomposition products is methane, with carbon dioxide and ethane in second and third places. Ethylene and propane are formed in smaller amounts. Acetone and tert-butyl alcohol are the main components of the decomposition products which are liquid under normal conditions. Methyl ethyl ketone, propionic acid methyl ester, acetic acid ethyl ester, and tert-butyl methyl ether can be detected in small concentrations. The oligomers of the solvent are also present.

The amount of gaseous decomposition products formed decreases with an increasing peroxide concentration of the solutions fed into the flow reactor. The decrease in the amount of methane and carbon dioxide formed per mole of decomposed peroxide is particularly strong when the peroxide concentration is increased from 1 to 5% by weight

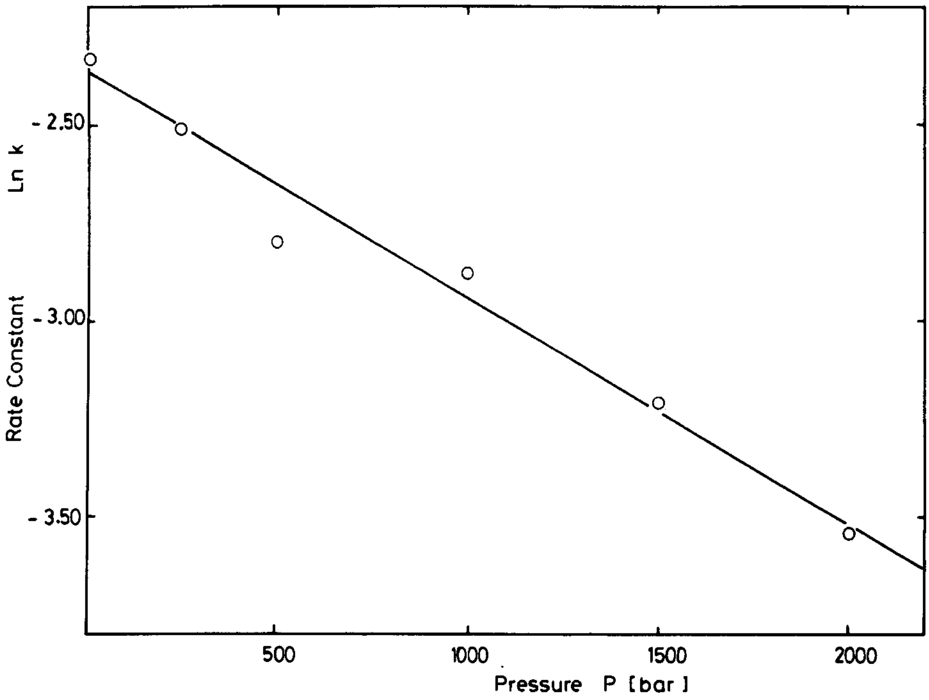


FIG. 5. Influence of the pressure on the rate constant of peroxide decomposition. Temperature: 200°C. Concentration of peroxide: 1 wt%.

TABLE 3. The Main Decomposition Products of 2,2-Bis(tert-butylperoxy)butane

Gaseous	Liquid
Methane	Acetone
Carbon dioxide	tert-Butyl alcohol
Ethane	Methyl ethyl ketone
Ethylene	Propionic acid methyl ester
Propane	Acetic acid ethyl ester tert-Butyl methyl ether Oligomers of isododecane

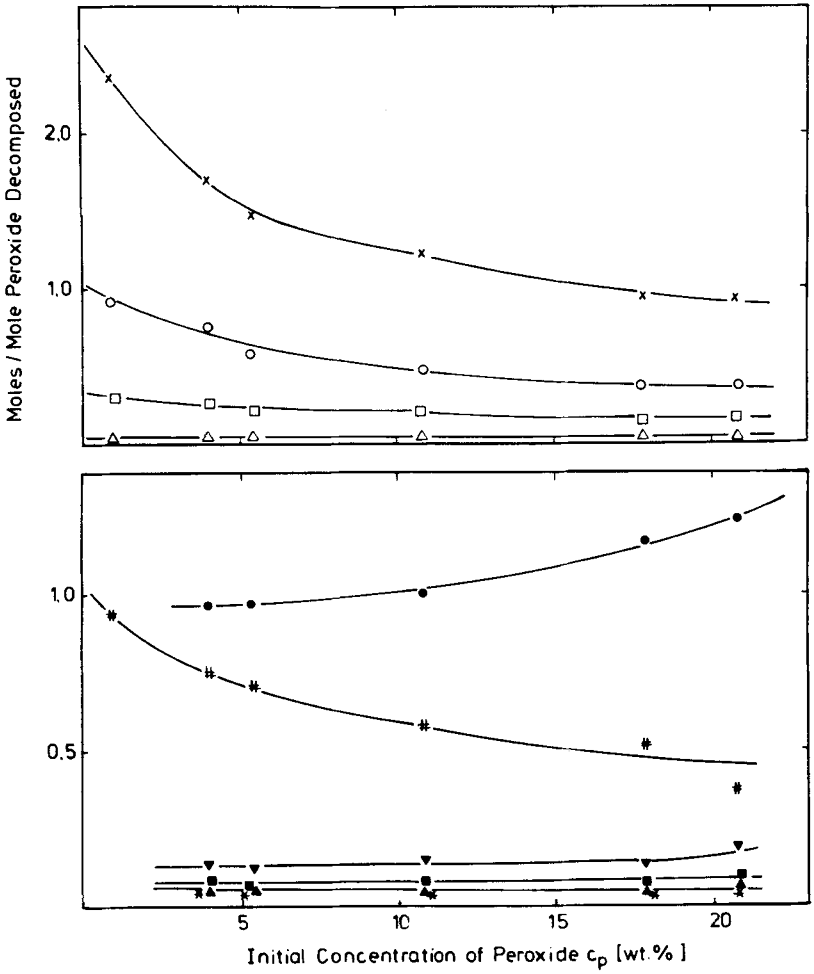


FIG. 6. Amount of gaseous and liquid decomposition products with varying concentration of peroxide. Temperature: 200°C. Pressure: Ambient. Above: Gaseous products, (×) methane, (○) carbon dioxide, (□) ethane, (△) ethylene. Below: Liquid products, (●) acetone, (#) tert-butyl alcohol, (▼) methyl ethyl ketone, (■) propionic acid methyl ester, (▲) acetic acid ethyl ester, (★) tert-butyl methyl ether.

(Fig. 6, top). The correlation between the formation of acetone as well as tert-butyl alcohol and the peroxide concentration is particularly striking in the case of the liquid decomposition products (Fig. 6, bottom). The quantities of the other liquid decomposition products formed remain almost constant. Methyl ethyl ketone and propionic acid methyl ester increase slightly with high peroxide concentrations while the quantities of acetic acid ethyl ester and tert-butyl methyl ether remain unchanged or decrease slightly.

The proportion of gaseous decomposition products decreases with rising pressure (Fig. 7, left-hand side). The effect of the pressure becomes fairly noticeable only at pressures above 250 to 500 bar, particularly in the case of methane and carbon dioxide. As regards the liquid decomposition products, the formation of tert-butyl alcohol is increased by high pressure; that of acetone is reduced (Fig. 7, right-hand side). The quantities of propionic acid methyl ester and

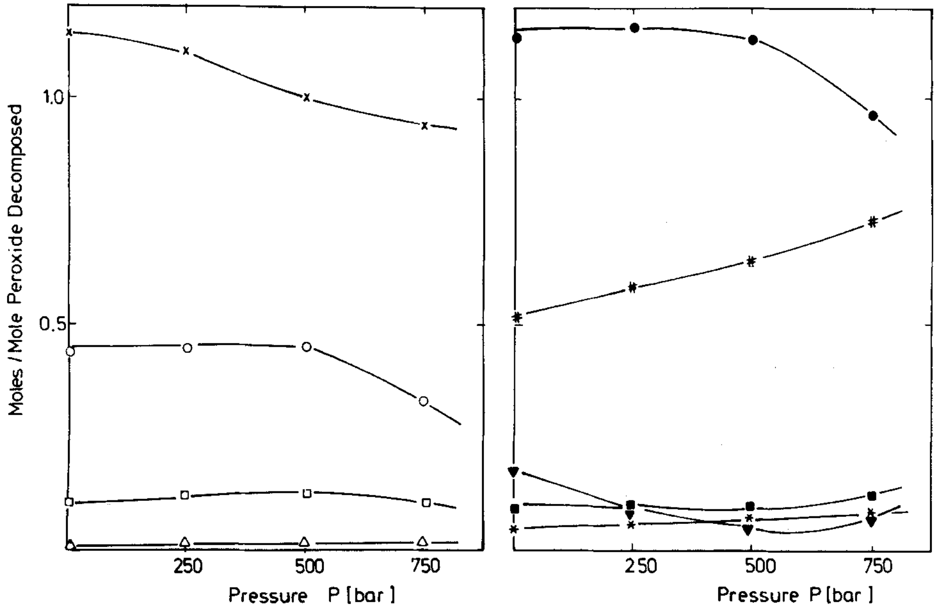


FIG. 7. Product spectra at different pressures. Temperature: 200°C. Concentration of peroxide: 21.75 wt%. Left: Gaseous products, (×) methane, (○) carbon dioxide, (□) ethane, (△) ethylene. Right: Liquid products, (●) acetone, (#) tert-butyl alcohol, (▼) methyl ethyl ketone, (■) propionic acid methyl ester, (★) tert-butyl methyl ether.

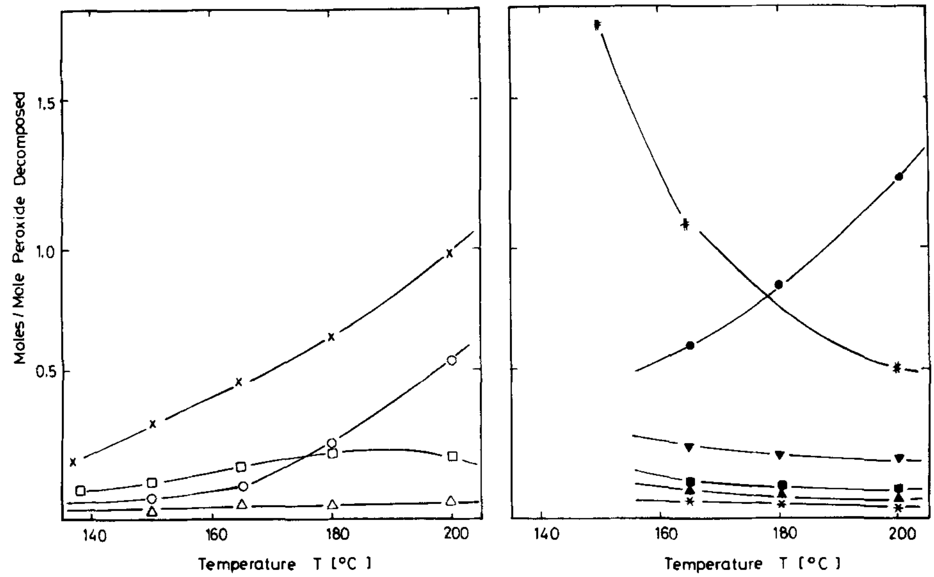


FIG. 8. Product spectra at different temperatures. Pressure: Ambient. Concentration of peroxide: 21.75 wt%. Left: Gaseous products, (×) methane, (○) carbon dioxide, (□) ethane, (△) ethylene. Right: Liquid products, (●) acetone, (#) tert-butyl alcohol, (▼) methyl ethyl ketone, (■) propionic acid methyl ester, (▲) acetic acid ethyl ester, (★) tert-butyl methyl ether.

tert-butyl methyl ether increase slightly. The proportion of methyl ethyl ketone decreases initially with increasing pressure and increases again subsequently.

The changes in the product spectrum as a function of the temperature are illustrated in Fig. 8. Under normal pressure and with high peroxide concentrations of 21.8% by weight, the formation of methane and carbon dioxide gas increases with the temperature. The proportion of ethane and ethylene remains almost constant (Fig. 8, left-hand side). At low temperatures the formation of acetone is promoted. Initially, the amount of tert-butyl alcohol is relatively small; however, it increases when the temperature is raised. On the other hand, the amount of acetone formed per mole of decomposed peroxide increases with rising temperatures. The proportion of methyl ethyl ketone and of the other identified liquid decomposition products, namely propionic acid methyl ester, acetic acid methyl ester, and tert-butyl methyl ether, decreases slightly at high temperatures (Fig. 8, right-hand side).

Finally, the influence of the residence time was investigated. The longer the peroxide and its decomposition products remain in the flow

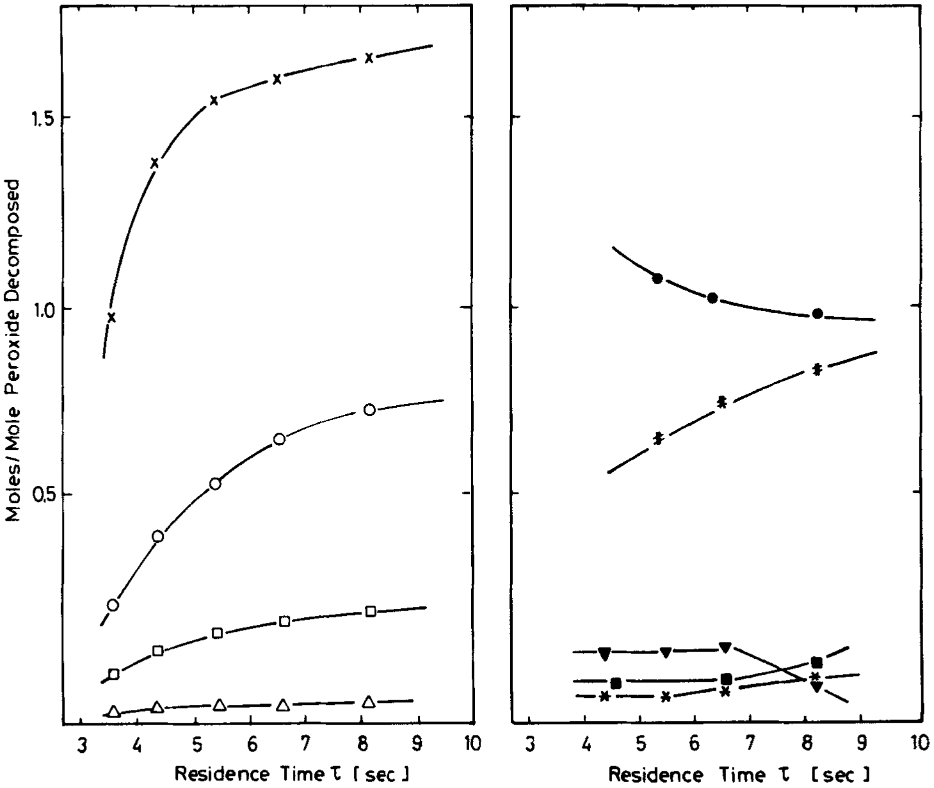


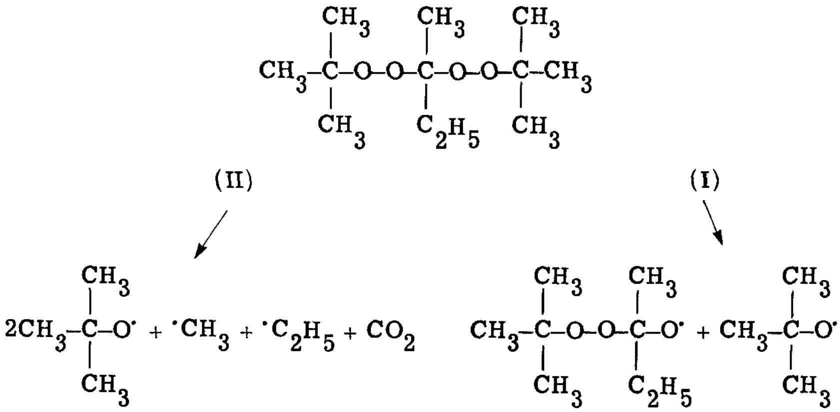
FIG. 9. Influence of the residence time on the composition of the decomposition products. Temperature: 200°C. Pressure: Ambient. Concentration of peroxide: 4.0 wt%. Left: Gaseous products, (×) methane, (○) carbon dioxide, (□) ethane, (△) ethylene. Right: Liquid products, (●) acetone, (#) tert-butyl alcohol, (▼) methyl ethyl ketone, (■) propionic acid methyl ester, (★) tert-butyl methyl ether.

reactor at high temperatures, the greater the proportion of gaseous components becomes (Fig. 9, left-hand side). Changing the residence time affects the formation of the various liquid decomposition products differently (Fig. 9, right-hand side). Increasing the residence time causes the proportion of acetone formed to decrease and the amount of tert-butyl alcohol to increase strongly initially and less strongly subsequently. The proportion of propionic acid methyl ester and tert-butyl methyl ether also increase while the proportion of methyl ethyl ketone decrease at high residence times.

DECOMPOSITION MECHANISM

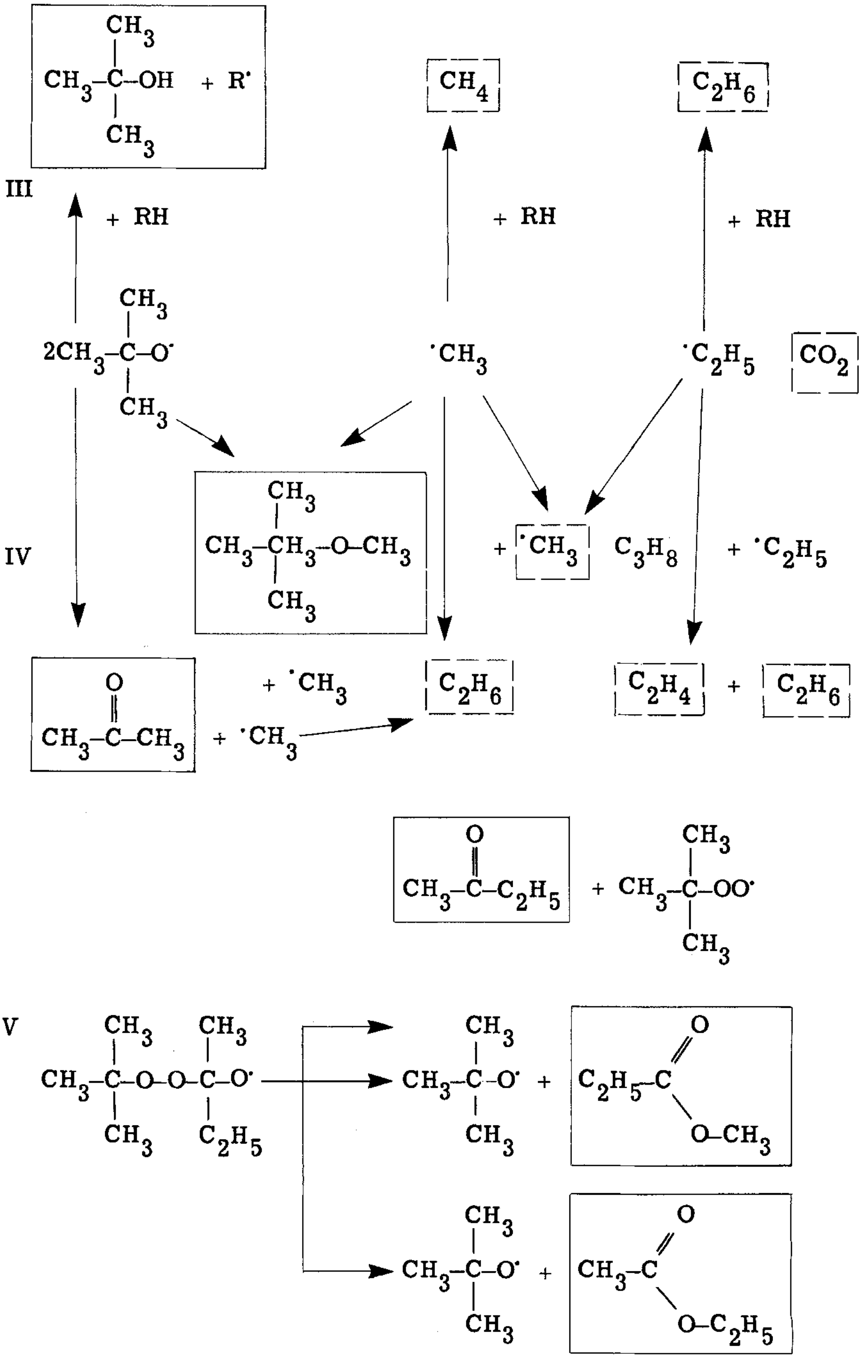
The mechanism suggested below for the decomposition provides an explanation for the decomposition products obtained. For clarity's sake, the gaseous decomposition products are boxed with a broken line, the liquid products with a solid line.

The bifunctional peroxide is capable of decomposing stepwise as shown by Bukata et al. [10] for the decomposition of a structurally similar compound, namely n-butyl-4,4-bis(tert-butylperoxy)valerate. In this way (I), two radicals are formed by one O–O bond being split initially. Another possibility is the concerted decomposition (II) into several radical fractions and carbon dioxide.



The radicals formed are capable of decomposing further, combining with each other or reacting with the solvent (RH). The courses of reaction at the top of page 1197 are open to the fractions of concerted decomposition by means of which the liquid reaction products tert-butyl alcohol, acetone, and tert-butyl methyl ether are formed. This also explains the formation of the gases methane, ethane, propane, and ethylene. It was not possible to detect the formation of butane as a result of the recombination of two ethyl radicals or that of tert-butyl ethyl ether by the combination of a tert-butoxy and an ethyl radical.

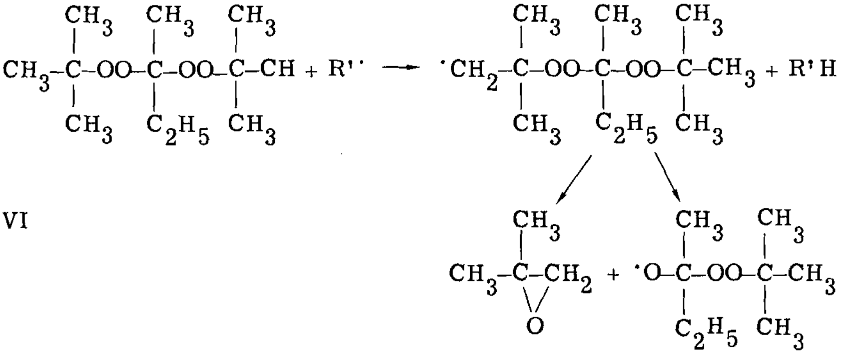
As a result of the subsequent decomposition of the fractions formed by reaction (I), the same products are formed from carbon dioxide, tert-butoxy, methyl, and ethyl radicals as those obtained from the concerted decomposition offering the same possibilities of reaction. In addition, the following courses of reaction are possible which give methyl ethyl ketone as well as propionic acid methyl ester and acetic acid ethyl ester.


III
CH3–C(CH3)2–OH + R•
+ RH
CH4
+ RH
C2H6
+ RH
2CH3–C(CH3)2–O•
•CH3
•C2H5
CO2
IV
CH3–C(CH3)2–O–CH3
+ •CH3
C3H8
+ •C2H5
CH3–CO–CH3
+ •CH3
+ •CH3
C2H6
C2H4
+
C2H6
CH3–CO–C2H5
+ CH3–C(CH3)2–OO•
V
CH3–C(CH3)2–O–O–C(CH3)(C2H5)–O•
CH3–C(CH3)2–O• + C2H5–C(=O)–O–CH3
CH3–C(CH3)2–O• + CH3–C(=O)–O–C2H5

The products with a relatively high molecular weight are oligomers of the solvent used, and are formed from the solvent radicals $R^{\cdot}$ after the abstraction of hydrogen:

$$R^{\cdot} + R^{\cdot} \longrightarrow R_2$$

In the case of the induced decomposition, the peroxide molecule is attacked by the radical R':

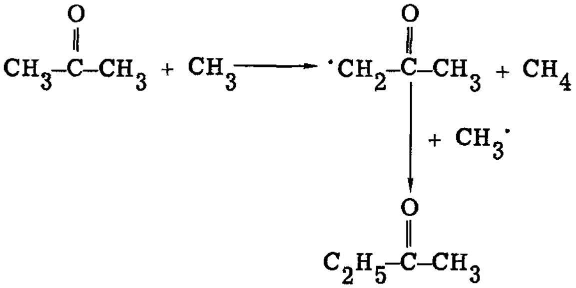


VI

During the subsequent reaction, the same peroxide radical is formed, apart from i-butylene oxide, as during the noninduced stepwise decomposition (I) of the original peroxide. The i-butylene oxide could not be clearly allocated to one of the peaks occurring in the gas chromatograms of the decomposition products obtained from the experiments with high peroxide concentrations.

CONCLUSIONS

The relatively high positive volume of activation suggests participation of the concerted decomposition which is characterized by a fairly substantial increase in volume in the transition state. Because of the increased volume effect, the concerted decomposition (Route II) is more strongly inhibited at higher pressures than the stepwise decomposition (Route I). All the other reactions during which bonds are split are inhibited at high pressure because the volume increases in the transition state according to Eq. (4). Reaction stages involving the formation of new bonds such as combination reactions and reactions with the solvent, on the other hand, are promoted by increasing pressure. This explains the decrease in the gaseous decomposition products observed—with the exception of ethane—and the change in the proportion of the liquid components acetone and tert-butyl alcohol. The fact that *the amount of propionic acid methyl ester and tert-butyl methyl ether* increases with rising pressure can be explained by the lower level of inhibition on the stepwise decomposition exerted under high pressure. The initial decrease in the amount of methyl ethyl ketone formed could be attributable to the participation of the previously ignored radical reactions



$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 + CH_3 \longrightarrow {}^{\cdot}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 + CH_4$$

$$\Big\downarrow + CH_3^{\cdot}$$

$$C_2H_5{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$$

in the formation of the ketone. Since fewer methyl radicals are formed as a result of the pressure-induced inhibition of the decomposition reactions, the proportion of the methyl ethyl ketone formed by the above route should decrease with rising pressure.

The change in the product spectrum observed with changing temperature is due to the different levels of energy of activation in the reaction steps concerned. Consequently, the concerted decomposition and the attack of the radicals on the solvent or the peroxide molecule will be stronger at elevated temperatures. This explains the increased proportion of gaseous decomposition products at high temperatures. The formation of ethane increases only slightly since the combination of radicals is hardly influenced by the temperature. The formation of acetone and tert-butyl alcohol takes place in two competing steps:

IV $(CH_3)_3CO^{\cdot} \longrightarrow (CH_3)_2CO + CH_3^{\cdot}$

III $(CH_3)_3CO^{\cdot} + RH \longrightarrow (CH_3)_3COH + R^{\cdot}$

The energy of activation of the first of these two reactions should be approximately 40 kJ/mol higher [11]; it should therefore take preference at higher temperatures. This would explain the increase in the acetone level compared with the amount of tert-butyl alcohol at rising temperatures.

Induced decomposition (VI) occurs at high peroxide concentrations. As explained above, it produces intermediate products similar to those obtained by stepwise decomposition. Consequently, the reactions that are relevant in the latter case occur to an increased extent which explains the increase in the formation of methyl ethyl ketone, propionic acid methyl ester, acetic acid ethyl ester, and tert-butyl methyl ether.

The ratio of acetone to tert-butyl alcohol is again determined by the competition between the decomposition of the tert-butoxy radical into acetone and a methyl radical (IV) and the reaction (III) with the solvent. Because of the low level of solvent concentration, the rate of reaction of the latter step decreases, so that less alcohol is formed.

At a given peroxide concentration in the feed, the residual peroxide concentration at the flow reactor outlet is lower in the case of a longer residence time of the component in the reactor and vice versa. In view of this connection, it is possible to use the same arguments for establishing a correlation between the product spectrum and the residence time as those used when considering the influence of the peroxide concentration.

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