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# MECHANISM OF THE THERMAL DECOMPOSITION OF POLYSTYRENE PEROXIDE

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The thermal degradation of polystyrene peroxide was carried out using differential scanning calorimetry. The activation energy ($E$) was found to be 136 kJ mole$^{-1}$ at all extents of decomposition. The $E$ value was found to correspond to —O—O— dissociation. The order of reaction was found to decrease from 2 to 1 as the decomposition progresses, and the mechanism of the changeover was explained.

The nuclear magnetic resonance spectra (NMR), differential thermal analysis (DTA) and differential scanning calorimetric (DSC) analysis of pure polystyrene (PSP) have recently been reported [1]. Further, the kinetics of PSP decomposition have been studied by isothermal thermogravimetry (TG) [2]. The activation energy ($E$) was found to be 136 kJ mole$^{-1}$ and it was suggested that the rate-controlling step is —O—O— bond dissociation [2]. The order of reaction ($n$) and the detailed mechanism for pure PSP decomposition have not been reported so far.

It has been shown that DSC can be used to study the kinetics of the process and that $E$ can be derived without recourse to kinetic assumptions [3]. PSP decomposition was carried out by using the DSC technique (Perkin—Elmer DSC-1B), and the kinetic parameters such as $E$ and $n$ were evaluated to understand the mechanism.

The details of the operation of the instrument and the derivation of the fraction decomposed ($\alpha$) *vs.* time ($t$) or *vs.* temperature ($T$) plots from the thermal curves are described elsewhere [3]. Thermal curves obtained in the scanning modes were used for kinetic analysis. The shapes of the DSC curves of PSP can be seen elsewhere [1].

$E$ was calculated by using the following equation:

$$\frac{S}{\Delta H} = (1 - \alpha)^n A e^{-E/RT} \tag{1}$$

where $S$ is the DSC signal in millicalories per second for full-scale deflection, $\Delta H$ is the total heat of PSP decomposition, $A$ is the frequency factor and $R$ is the gas constant. From Eq. (1), $E$ was obtained by plotting $\ln \frac{S}{\Delta H}$ *vs.* $\frac{1}{T}$. In doing so, $\alpha$ and $n$ were kept constant. $\alpha$ was fixed at a definite value for the curves at different heating rates, and the constancy of $n$ was checked from the reduced-time plots

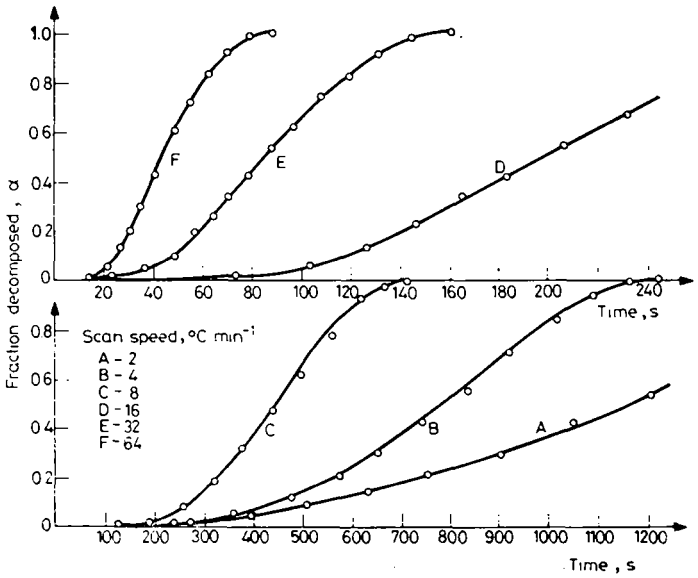



Fig. 1. Fraction decomposed *vs.* time plot for the thermal decomposition of polystyrene peroxide at different heating rates. Scan speed (° $min^{-1}$): A — 2, B — 4, C — 8, D — 16, E — 32, F — 64

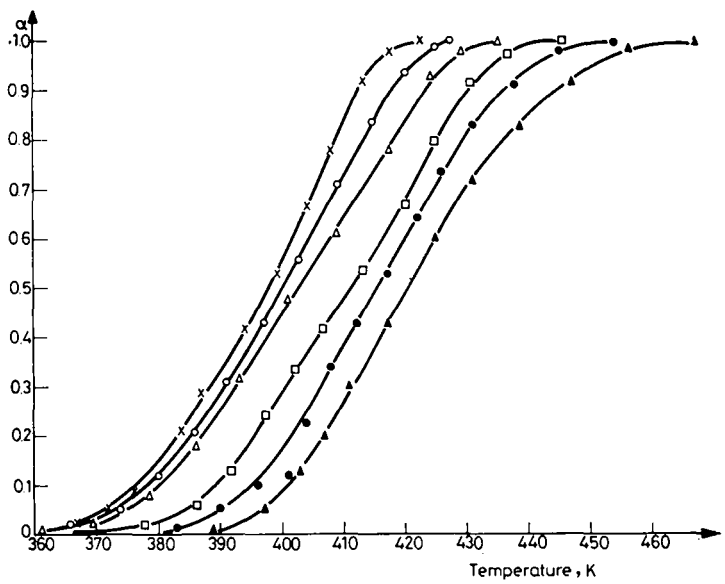



Fig. 2. Fraction decomposed (α) *vs.* temperature plots at different heating rates. Scan speed (° $min^{-1}$): × — 2, ○ — 4, △ — 8, □ — 16, ● — 32, ▲ — 64

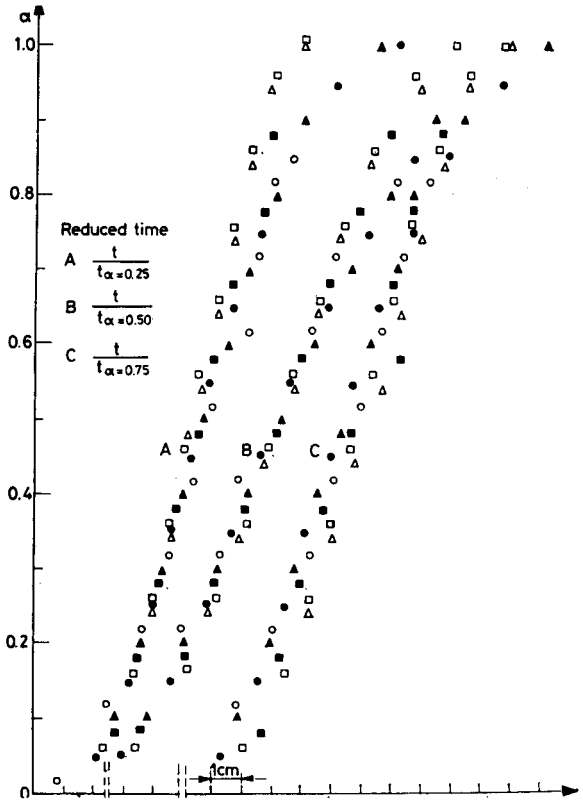



Fig. 3. Fraction decomposed *vs.* reduced time plots at various stages of reaction. Scan speed (° min$^{-1}$): ○ 2; △ 4; □ 8; ■ 16; ▲ 32; ● 64

[4]. The $\alpha$ vs. $t$, $\alpha$ *vs.* $T$ and $\alpha$ *vs.* reduced-time plots (at different $\alpha$ values) are shown in Figs 1, 2 and 3, respectively.

From Fig. 3 it is clear that the mechanism of the reaction does not alter with the heating rate, and therefore $n$ is constant for a given $\alpha$ value. The $E$ values were obtained at $\alpha = 0.2, 0.4, 0.6$ and 0.8. The average $E$ value was found to be $136 \pm 9$ kJ mole$^{-1}$. This shows that the $E$ value does not change at different extents of decompositions, and also that it tallies well with the bond dissociation energy of the $-O-O-$ bond. This strongly confirms that the rate-controlling step involves dissociation of the $-O-O-$ linkage.

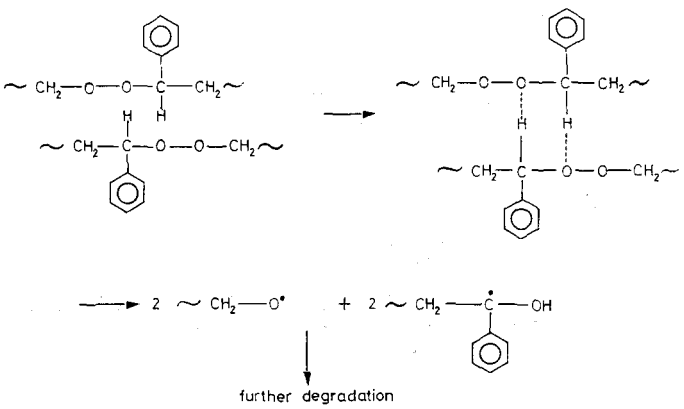
From Eq. (1), $n$ was calculated at 405, 410 and 415 K from the slope of the plot of ln $S/\Delta H$ *vs.* ln $(1 - \alpha)$. The data were taken from Fig. 2. It was found that $n$ is 2 at 405 K, 1.8 at 410 K and 1.2 at 415 K. This result shows that the order of reaction changes with temperature, i.e. as the reaction proceeds $n$ decreases from 2 to 1. Since $E$ remains constant throughout the entire reaction region, the observed change in $n$ suggests that altough the rate-controlling step is the dissociation of the

$-O-O-$ linkage the actual mode of dissociation changes during the course of decomposition.

It has been proposed by Shelton and Vincent [5] that hydroperoxide decomposition can be second-order when the hydroperoxide concentration is high. They explained the occurrence of bimolecular decomposition on the basis of hydrogen-bonding, as shown below:

$$\begin{array}{l} 2\,ROOH \rightarrow 2\,RO^0 + 2\,HO^0 \\ \quad\uparrow\downarrow \\ \quad ROOH \\ \qquad\;\; | \\ \qquad\;\; HOOR \rightarrow RO^0 + RO_2^0 + H_2O. \end{array}$$

In PSP, such a type of hydrogen-bonding cannot be envisaged. The only way by which bimolecular decomposition could be explained is as follows:




The interaction between the oxygen and hydrogen atoms as shown in the above scheme seems plausible, because the ternary hydrogen atom in PSP is quite labile. This type of decomposition is similar to the decomposition on of HI, and PSP decomposition in such a mode is possible because the $-O-O-$ bonds are in-bonded in the chain. As the concentration of the peroxide goes on decreasing during the progress of the reaction, the probability of two peroxide linkages coming together continuously decreases. However, since the reaction is exothermic in nature, and once initiated the dissociation of the peroxide could be possible without bimolecular collisions, unimolecular decomposition can therefore occur. Bimolecular reactions generally occur in gaseous and liquid-phase reactions. PSP is viscous at room temperature, but as the temperature is increased for decomposition to occur the viscosity decreases and the significant movement of the polymer segments is possible. The changeover of $n$ from 2 to 1 can be explained on the

basis of the above facts. A careful examination of the shape of the DSC curve (1) shows clearly that the decomposition is complex and involves the changeover of the mechanism after the decomposition has proceeded to a certain extent.

## References

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RÉSUMÉ — La dégradation thermique du peroxyde de polystyrène a été examinée par DSC. On a trouvé que l'énergie d'activation ($E$) s'élevait à 136 kJ mole$^{-1}$ pour tous les stades de la décomposition et qu'elle correspondait à la dissociation —O—O—. L'ordre de la réaction diminue de 2 à 1 au fur et à mesure de l'avancement de la décomposition. Le mécanisme de ce changement est expliqué.

ZUSAMMENFASSUNG — Die thermische Zersetzung von Polystyrolperoxid wurde unter Anwendung der Differential-Scanning-Kalorimetrie durchgeführt. Bei allen Zersetzungsgraden wurde eine Aktivierungsenergie ($E$) von 136 kJ Mol$^{-1}$ gefunden. $E$ entspricht der —O—O— Dissoziation. Es wurde festgestellt, daß sich die Reaktionsordnung mit vortschreitender Zersetzung von der zweiten auf die erste herabsetzt und der Mechanismus der Änderung wurde erklärt.

Резюме — С помощью дифференциальной сканирующей калориметрии изучено термическое разложение перекиси полистирола. Найдено, что на всех ступенях разложения энергия активации ($E$) равна 136 кдж.моль$^{-1}$. Установлено, что энергия активации $E$ соответствует диссоциации связи —O—O—. Найдено, что порядок реакции уменьшается от 2 до 1, что было объяснено изменением как хода разложения, так и его механизма.