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Abstract

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CHEMISTRY

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ON THE MECHANISM OF THERMAL DESTRUCTION OF CURED EPOXY RESINS

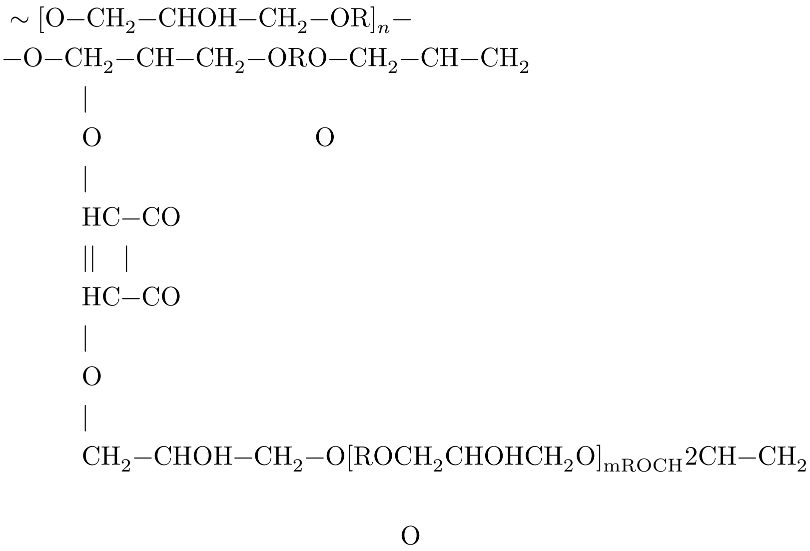
(Presented by Academician V. A. Kargin, 29 VI 1960)

As is known, the thermal destruction of polymers is a radical-chain process (1). A large number of indirect experimental data speak in favor of these concepts. After the appearance and broad development of the method of electron paramagnetic resonance (EPR), which makes it possible to detect radicals at concentrations greater than $5 \cdot 10^{13}$ g, it became possible to study the mechanism of polymer destruction by a direct method.

In the present work we studied the kinetics of thermal destruction of epoxy resins cured with maleic anhydride and polyethylene-polyamine. An attempt was also made to determine the radicals formed by the EPR method.

The kinetics of thermal destruction of epoxy resins was studied by three methods: by gas evolution, by loss in weight of the residue, and by determining radicals by the EPR method. The results obtained by us are shown schematically in Fig. 1. An attempt to detect radicals by the EPR method gave a positive result only at later stages of the course of the process.

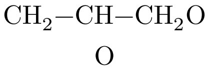
Analysis of the gaseous products showed the presence of considerable amounts of methane, carbon monoxide, formaldehyde, acetaldehyde, and acrolein. Gas evolution, depending on the temperature, practically ceases 5–15 min after the start of the reaction. However, the process of thermal destruction continues, and liquid products of comparatively low molecular weight are distilled off from the polymer. Below is shown the structure of the molecule of the epoxy resin cured with maleic anhydride



$$\begin{array}{l}
\sim[O-CH_2-CHOH-CH_2-OR]_n- \\
-O-CH_2-CH-CH_2-ORO-CH_2-CH-CH_2 \\
\qquad\quad | \\
\qquad\quad O \qquad\qquad\qquad\qquad\qquad O \\
\qquad\quad | \\
\qquad\quad HC-CO \\
\qquad\quad || \quad | \\
\qquad\quad HC-CO \\
\qquad\quad | \\
\qquad\quad O \\
\qquad\quad | \\
\qquad\quad CH_2-CHOH-CH_2-O[ROCH_2CHOHCH_2O]_{mROCH}2CH-CH_2 \\
\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad O
\end{array}$$

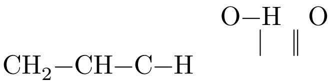
$$R = -\between-C(CH_3)_2-\between-$$

We suppose that the terminal groups



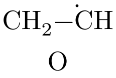
$$\begin{array}{c} CH_2-CH-CH_2O \\ O \end{array}$$

are most readily detached from the polymer. This radical may isomerize into the radical



$$\begin{array}{l} \qquad\qquad\qquad\quad O-H \quad O \\ \qquad\qquad\qquad\qquad | \quad\; \| \\ CH_2-CH-C-H \end{array}$$

from which acrolein and hydroxyl are formed. In addition, the primary radical may decompose into a molecule of CH_2O and the radical



$$\begin{array}{c} CH_2-\dot{C}H \\ O \end{array}$$

As a result of isomerization of this radical, an acetyl radical $CH_3-\dot{C}O$ may be obtained, which, abstracting hydrogen from the epoxy resin, forms acetaldehyde. Finally, the acetyl radical may decompose into CO and $\dot{C}H_3$. The latter, by adding hydrogen, is converted into methane. The proposed scheme explains the formation of all the products found in the gas phase during the thermal

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

decomposition of the epoxy resin. Besides detachment of terminal groups, bonds between carbon atoms in the aliphatic portions of the epoxy-resin chains may also be broken. In this case volatile products of low molecular weight may be formed.

Fig. 1. Scheme of the kinetics of the processes during thermal decomposition of cured epoxy resins: gas evolution (1), weight loss (2), accumulation of radicals (3)

In all the cases considered, the reaction proceeds through active radicals, which cannot accumulate in large concentrations; therefore they cannot be detected by the EPR method.

However, rupture of such bonds of diphenylolpropane is also possible, leading to the formation of stable radicals. The latter may accumulate in high concentrations and can readily be detected by the EPR method. It is possible that the formation of stable radicals during the thermal destruction of cured epoxy resins occurs as a result of cleavage of the phenyl-carbon bond, which leads to the formation of semiquinone structures. The singlet signals of radicals observed by us are shown in Fig. 2. They have the same appearance as the signals obtained by Ingram (2) in studying the destruction of coals, by Berlin and Blumenfeld (3,4), by Topchiev (5) and Voevodskii (6) in studying polymers with a system of conjugated bonds, and also a number of carbonized materials. The radicals recorded by us live for a very long time: their concentration changes comparatively little over the course of a month (at room temperature).

Fig. 2. Example of the signal of stable radicals formed during the decomposition of cured epoxy resins. Signal width 10 oersteds.

Figure 3 shows the kinetics of accumulation of stable radicals during the thermal decomposition of epoxy resins cured with maleic anhydride (Fig. 3a) and polyethylene polyamine (Fig. 3b). We also obtained data on the kinetics of thermal decomposition of cured epoxy resins by gas evolution and by decrease in the weight of the residue over a broad temperature interval. The latter data were partially published (7,8).

The data obtained by us made it possible to estimate separately the activation energies of three parallel processes occurring during the thermal destruction of cured epoxy resins: the first—by gas evolution, the second—by weight loss of the residue, and the third—by the rate of accumulation of radicals.

Figure 3

Figure 3: Figure 3

Figure 4

Figure 4: Figure 4

Figure 4 shows the dependence of the rates of these processes on temperature in the coordinates $\lg \omega$ and $1/T$. It turned out that, in the case of thermal destruction of an epoxy resin cured with maleic anhydride, the activation energies of the first, second, and third processes are, respectively, 30, 26, and 53 kcal/mole, and, in the case of an epoxy resin cured with polyethylene polyamine, 25, 35, and 44 kcal/mole.

Fig. 3. Kinetics of accumulation of stable radicals during decomposition of epoxy resins cured with maleic anhydride (left) and polyethylene polyamine (right). **1, 4** were taken at 350°; **2, 5** at 375°; **3, 6** at 405°.

It may be assumed that the first two processes are associated with the rupture of less strong bonds, while the third is associated with the rupture of stronger bonds.

The experiments described have shown that, with the present-day EPR technique, it is difficult to detect active radicals, but the detection of low-activity radicals during the destruction of polymers is a feasible task.

Fig. 4. Dependence of the rate of thermal destruction of epoxy resins cured with maleic anhydride (left) and polyethylene polyamine (right) on temperature. **1, 4**—from the kinetics of gas evolution; **2, 5**—from the loss of weight; **3, 6**—from the rate of accumulation of stable radicals.

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REFERENCES

1. H. Grassie, *Chemistry of Polymer Degradation Processes*, IL, 1959.
2. D. J. E. Ingram, J. G. Tapley, *Chem. and Ind.*, 1955, p. 568.

3. A. A. Berlin, L. A. Blyumenfel'd et al., *Vysokomolek. soed.*, **1**, 1361 (1959).
4. L. A. Blyumenfel' d, A. A. Berlin et al., *Strukturnaya khimiya*, **1**, No. 1 (1960).
5. A. V. Topchiev, M. A. Genderikh et al., *DAN*, **128**, 3121 (1959).
6. V. V. Voevodskii, N. I. Tikhomirova, *Strukturnaya khimiya*, **1**, No. 1 (1960).
7. M. B. Neiman, L. I. Golubenkova et al., *Vysokomolek. soed.*, **1**, 1531 (1959).
8. M. B. Neiman, B. M. Kovarskaya et al., *Plasticheskie massy*, **1**, No. 7 (1960).

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