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**Abstract**

**Full Text**

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# Thermal Degradation of Polymers of Vinylphosphinic Acid Esters

The synthesis of polymers and copolymers of vinylphosphinic acid esters is of undoubted practical interest owing to the fact that many of them are capable of self-extinguishing when removed from a flame ([1,2]). We observed that the self-extinguishing ability of copolymers of vinylphosphinic acid esters with styrene depends not only on the phosphorus content in the copolymer, but also on the nature of the ester groups of the vinylphosphinic acid ester. In the case of dialkyl esters of vinylphosphinic acid, the copolymers acquired the ability to self-extinguish at a higher phosphorus content ($\geq 6\%$) than in the case of the diphenyl ester of vinylphosphinic acid, where the copolymers became self-extinguishing at a phosphorus content of about 4%. It should be noted that these tests were carried out with foams, i.e., on specimens with a developed surface.

Apparently, during the thermal decomposition of copolymers of styrene with alkyl esters of vinylphosphinic acid, volatile products are formed, the combustion of which releases heat sufficient for the decomposition of adjacent layers of the copolymer. Thus, with insufficient phosphorus content, combustion in this case will continue until the copolymer has burned completely. During the thermal decomposition of copolymers of styrene with the diphenyl ester of vinylphosphinic acid, volatile combustible products are formed in smaller amounts; mainly, a process of coking of the copolymer takes place.

In order to verify the validity of the above assumption and to determine the thermal stability of polymers of vinylphosphinic acid esters, we studied the thermal decomposition of these polymers. There are no data in the literature on the thermal degradation of polymers of vinylphosphinic acid esters.

The most probable decomposition appears to proceed according to the scheme:

$-CH_2 - CH- \longrightarrow -CH_2 - CH- \longrightarrow$

O // P, $RCH_2CH_2O/$ \O $- CH_2 - C(H)(R)H$ ; O⋯⋯H // \ P C(H)(R), $RCH_2CH_2O/$ \O $- CH_2/$

$\longrightarrow -CH_2 - CH-$ OH / P, $RCH_2CH_2O/$ \\O $+ CH_2{=}CHR$

Cleavage of the second molecule of olefin occurs in an analogous manner. Indeed, the only gaseous product formed when the polymer of di-*n*-propyl vinylphosphinate was heated at 180° in a weak stream of nitrogen for 10 hours proved to be propylene.

which was established by gas–liquid chromatography (KhL-3 chromatograph). The remaining polymer acquired an acidic character.

Chromatographic analysis of the gaseous decomposition products of polymers of the di-*n*-butyl, di-*n*-amyl, and other higher alkyl esters of vinylphosphinic acid showed that in these cases a mixture of isomers of the corresponding alkenes is formed; at the same time, acid groups are formed. Thus, after heating the polymers in sealed ampoules in a nitrogen atmosphere at 200° for two hours, the content of acid groups in the solid residue was:

| Polymer of the vinylphosphinic acid ester | Content of acid groups, of theoretical possible, % |
|---|---|
| di-*n*-butyl | 4.16 |
| diisobutyl | 7.71 |
| di-*n*-amyl | 4.28 |
| diisoamyl | 3.61 |
| di-*n*-heptyl | 5.14 |

From the data presented it is evident that polymers of *n*-alkyl esters of vinylphosphinic acid decompose the more readily, the larger the alkyl radical. The polymer of the diisobutyl ester of vinylphosphinic acid decomposes more readily than the polymer of the diisoamyl ester of vinylphosphinic acid, apparently because of the presence of a tertiary carbon atom in the $\beta$-position to this oxygen atom, which is consistent with the proposed decomposition scheme.

**Table 1**

**Decomposition of the polymer of the diisoamyl ester of vinylphosphinic acid**

| Time $\times 10^{-3}$, sec | Acid number, % of maximum possible | Decomposition rate $\times 10^{-4}$, {-1} | $K_1 \cdot 10^{-6}$, $sec^{-1}$ | Time $\times 10^{-3}$, sec | Acid number, % of maximum possible | Decomposition rate $\times 10^{-4}$, {-1} | $K_1 \cdot 10^{-6}$, $sec^{-1}$ |
|---|---|---|---|---|---|---|---|
| **At temperature 150°** | **At temperature 150°** | **At temperature 150°** | **At temperature 150°** | **At temperature 200°** | **At temperature 200°** | **At temperature 200°** | **At temperature 200°** |
| 10.8 | 0.80 | 0.62 | 0.75 | 1.8 | 1.8 | 10.8 | 10.2 |
| 21.6 | 1.40 | 0.62 | 0.53 | 3.6 | 4.08 | 10.8 | 11.5 |
| 32.4 | 1.84 | 0.62 | 0.58 | 7.2 | 7.7 | 10.8 | 11.1 |
| 43.2 | 2.67 | 0.62 | 0.62 | 10.8 | 10.8 | 10.8 | 10.6 |
| average | average | average | 0.62 | 14.4 | 15.8 | 10.8 | 11.8 |
| | | | | average | average | average | 11.0 |
| **At temperature 180°** | **At temperature 180°** | **At temperature 180°** | **At temperature 180°** | **At temperature 210°** | **At temperature 210°** | **At temperature 210°** | **At temperature 210°** |
| 7.2 | 2.2 | 2.9 | 3.14 | 1.8 | 3.1 | 15.2 | 17.5 |
| 14.4 | 4.1 | 2.9 | 2.90 | 3.6 | 5.9 | 15.2 | 17.9 |
| 21.6 | 6.0 | 2.9 | 2.94 | 5.4 | 7.85 | 15.2 | 15.1 |
| 28.8 | 8.3 | 2.9 | 3.15 | 7.2 | 10.95 | 15.2 | 16.1 |
| 36.0 | 10.4 | 2.9 | 3.05 | 9.0 | 16.15 | 15.2 | |
| average | average | average | 3.04 | average | average | average | 16.7 |

The thermal decomposition of the polymer of the diisoamyl ester of vinylphosphinic acid was studied in more detail. The polymer was heated in a weak stream of nitrogen; the extent of degradation was judged from the acid number, referred to the maximum possible acid number attained upon complete cleavage of the alkyl groups in the form of olefins. This control method proved more convenient and gave well reproducible results in comparison with measurement of the weight loss of the polymer. In the latter case, a change in weight is also recorded owing to anhydridization of the acid groups; in determining acid numbers, anhydridization of the acid groups has no effect on the results obtained, which are given in Table 1. This table gives the decomposition rates and the rate constants of the decomposition reaction, calculated as for a first-order reaction.

The average temperature coefficient of the reaction rate, calculated from the data given in Table 1, is 1.7, and the activation energy, determined graphically from the dependence of the reaction-rate constant on temperature in Arrhenius coordinates, is 22.3 kcal/mole.

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*Note: Figure translations are in progress. See original paper for figures.*