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Abstract

Full Text

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STUDY OF THE RATE OF THERMAL DECOMPOSITION OF UNSATURATED ORGANOSILICON PEROXIDES

(Presented by Academician V. N. Kondrat’ ev on 23 VIII 1963)

Organosilicon peroxide compounds have been known since 1954, and at present about thirty representatives have been obtained of types R_3SiOOH (A), $R_3SiOOSiR_3$ (B), or R_3SiOOR_1 (V). However, their thermal decomposition has not yet been systematically studied, and only general information is available on this question. In papers ([1],[3],[4],[9]) it is indicated that hydroperoxides of type A are unstable. For example, trimethylsilyl hydroperoxide already at 0° rapidly turns into a peroxide of hexamethyldisilane of type B.

Peroxides of type B are more stable, and their stability depends to a greater degree on the nature of the hydrocarbon radicals. For example, hexamethyldisilyl peroxide ([3],[7]) at 135° in isopropylbenzene decomposes twice as slowly as di-tert-butyl peroxide, which among organic peroxides is distinguished by very high stability, whereas hexaethyldisilyl peroxide, owing to decomposition, cannot be isolated in pure form by distillation at 0.01 mm Hg and 62° ([10]). Crystalline hexaphenyldisilyl peroxide ([1],[8]), isolated in pure form, decomposes by 50% in one day at room temperature.

Fig. 1. Thermal decomposition of unsaturated organosilicon peroxides *I*, *II*, *III*, and *IX* in isopropylbenzene at 130°

Most of the known peroxides belong to type V ([2],[3],[7],[8],[11–13]), among which peroxides containing organic tertiary radicals at the peroxide group are distinguished by enhanced stability, since tert-butyl, tert-amyl, and cumyl. These peroxides are preserved at room temperature for many months without noticeable decomposition.

With the aim of systematically studying the thermal stability of organosilicon peroxides, the present investigations were carried out on the rate of thermal decomposition of ten unsaturated organosilicon peroxides of mixed type V, obtained by us ([12],[13]), with one, two, and three peroxide groups at this silicon.

The investigations were conducted in sealed ampoules in a nitrogen atmosphere at 120, 130, and 140°, in the presence of the solvents isopropylbenzene, ethylbenzene, and toluene. For the experiments, solutions were taken containing 0.2 mole of active oxygen per liter of solution, and the decomposition was monitored by the iodometric method with addition of hydrochloric acid.

Investigation of the rate of thermal decomposition of monoperoxides. The following peroxides were subjected to thermal decomposition in isopropylbenzene: mono-tert-butyl peroxymethylvinylsilane
$CH_2{=}CH{-}Si(CH_3)(C_2H_5){-}OOC(CH_3)_3$ (I), mono-cumyl peroxymethylvinylethylsilane
$CH_2{=}CH{-}Si(CH_3)(C_2H_5){-}$

$OOC(CH_3)_2C_6H_5$ (II) and mono-tert-amylperoxymethylvinylsilane $CH_2{=}CH{-}Si(CH_3)(C_2H_5){-}OOC{-}(CH_3)_2C_2H_5$ (III). The results are shown in Fig. 1. Analytical treatment of the results obtained showed that the decomposition of unsaturated organosilicon monoperoxides does not obey a first-order equation, and, as is seen from Fig. 1, the decomposition rate decreases with time.

Gane and Mettinger, in work ([3]), also were unable to determine the rate constant for decomposition of a peroxide of this type—tert-butylperoxytrimethylsilane. The authors supposed that the products of peroxide decomposition interact with hydroiodic acid. It seems to us that the reasons for the failure of mixed organosilicon peroxides to undergo monomolecular decomposition are still not clear.

However, the results shown in Fig. 1, in comparison with the data of other authors ([3]), show that the unsaturated monoperoxides studied by us (especially I and II) are more stable than the symmetrical saturated hexamethyldisilyl peroxide and di-tert-butyl peroxide. It is interesting to note that on going to peroxide III with a tert-amyl radical, the thermal stability of the latter decreases considerably.

By the transformation method of Emanuel ([14]), the overall activation energies E of peroxide decomposition were calculated, giving the following results: for I, 30.4; II, 28.0; and III, 26.3 kcal/mole.

Study of the rate of thermal decomposition of peroxides. The following diperoxides were investigated: di-tert-butylperoxymethylvinylsilane $CH_2{=}CH{-}Si(CH_3)[{-}OOC(CH_3)_3]_2$ (IV), di-tert-butylperoxyvinylethylsilane $CH_2{=}CH{-}Si(C_2H_5)[{-}OOC(CH_3)_3]_2$ (V), di-tert-butylperoxyvinylpropylsilane $CH_2{=}CH{-}Si(C_3H_7){-}[{-}OOC(CH_3)_3]_2$ (VI), di-tert-amylperoxymethylvinylsilane

Fig. 2. Thermal decomposition of unsaturated organosilicon diperoxides IV, V, VI, VII, VIII and trioxide X in isopropylbenzene at 130°

Figure 2: Fig. 2. Thermal decomposition of unsaturated organosilicon diperoxides IV, V, VI, VII, VIII and trioxide X in isopropylbenzene at 130°

$CH_2{=}CH{-}Si(CH_3)[{-}OOC(CH_3)_2C_2H_5]_2$ (VII), di-tert-amylperoxyvinylpropylsilane $CH_2{=}CH{-}Si(C_3H_7)\cdot[{-}OOC(CH_3)_2C_2H_5]_2$ (VIII), and di-tert-butylperoxymethylallylsilane $CH_2{=}CH{-}CH_2{-}Si(CH_3)[{-}OOC(CH_3)_3]_2$ (IX).

Fig. 2. Thermal decomposition of unsaturated organosilicon diperoxides IV, V, VI, VII, VIII and trioxide X in isopropylbenzene at 130°

Table 1

Rate constants K_1 and activation energies E for decomposition of unsaturated organosilicon peroxides in isopropylbenzene

Peroxide	K_1, h^{-1} at 120°	K_1, h^{-1} at 130°	K_1, h^{-1} at 140°	E, kcal/mole
IV	0.00535	0.0146	0.0368	31.1
V	0.0177	0.0409	0.0934	26.9
VI	0.00453	0.0126	0.0323	31.7
VII	0.00950	0.0234	0.0566	28.8
VIII	0.00794	0.0200	0.0495	29.5
X	0.0669	0.156	0.345	26.5

Thermal decomposition was carried out in isopropylbenzene, and decomposition of peroxide IV additionally in ethylbenzene and toluene. The data obtained are shown in Fig. 2, and the numerical values of the rate constants K_1 and activation energies E of thermal decomposition in isopropylbenzene are given in Table 1.

It is seen from Fig. 2 that, in contrast to the monoperoxides, the thermal decomposition of diperoxides and triperoxides follows the law of a monomolecular reaction, and therefore it is possible to carry out a more detailed analysis of the decomposition of these peroxides. Thus, for diperoxide IV, decomposition was carried out at different initial concentrations of 0.2 and 0.4 mole of active oxygen per liter of solution, and, according to Nozaki and Bartlett (15), the fraction of induced decomposition was determined; the results of these determinations are given in Table 2.

The data in Table 2 show that the apparent first-order rate constants K_1 increase as the initial diperoxide concentration is raised from 0.2 to 0.4 mole of active oxygen per liter of solution. The constants of true monomolecular dissociation K_d, calculated by the graphical method (15), are expressed by smaller numerical values, whereas the constants of induced decomposition

Table 2

Rate constants and activation energies for the decomposition of di-tert-butyl peroxymethylvinylsilane in various solvents and at different initial concentrations

Solvent	Initial conc., mol. $[O]$/l	Rate constants	at 120°	at 130°	at 140°	E, kcal/mol
Isopropylbenzene	0.2	K_1, h^{-1}	0.00535	0.0146	0.0368	31.1
Isopropylbenzene	0.4	K_1, h^{-1}	0.00649	0.0174	0.0433	30.6
Isopropylbenzene	0.4	K_d, h^{-1}	0.00160	0.00589	0.0189	39.8
Isopropylbenzene	0.2 and 0.4	K_i, $\left(\frac{\text{mol}}{\text{l}}\right)^{1/2}$ h^{-1}	0.00848	0.0208	0.0478	27.8
Isopropylbenzene	0.2 and 0.4	K_d/K_i	0.1887	0.2830	0.3950	–
Ethylbenzene	0.2	K_1, h^{-1}	0.00808	0.0211	0.0535	30.5
Toluene	0.2	K_1, h^{-1}	0.0139	0.0362	0.0883	29.8

K_i are expressed by larger numerical values for the temperatures studied. Thus, the thermal decomposition of the diperoxides proceeds to a considerable extent by the mechanism of induced decomposition.

In connection with the presence of induced decomposition, the data given in Table 2 on the influence of solvents on the decomposition of diperoxide IV are of interest. They show that the decomposition rate constants K_1 increase in the solvent series: isopropylbenzene < ethylbenzene < toluene. This sequence agrees with the data of the investigators (16) on the reactivity of the indicated hydrocarbons toward hydrogen abstraction by the tert-butoxyl $(CH_3)_3\dot{C}O$ radical in the order isopropylbenzene : ethylbenzene : toluene = 1 : 0.42 : 0.11. It follows from this that the rate of decomposition of the diperoxide increases as the activity of the solvent decreases, which is consistent with the presence of induced decomposition, which is inhibited by an active solvent to a greater extent than by a less active one. This is also confirmed by the activation-energy data, which decrease as the activity of the solvent decreases, where the fraction of induced decomposition is higher.

At the same time, the organosilicon diperoxides we have studied exceed organic diperoxides in thermal stability by almost two orders of magnitude. For example, according to the data of Dickey et al. (17), 2,2-di-tert-butylperoxybutane $CH_3—CH_2—C(CH_3)—[-OOC(CH_3)_3]_2$ decomposes at 120° in isopropylbenzene with a rate constant of 0.46 h^{-1}, whereas according to our data the analogous organosilicon di-tert-butyl peroxymethylvinylsilane IV has 0.00535 h^{-1}.

Organosilicon diperoxides also exceed organic dialkyl monoperoxides in thermal stability. For example, diperoxide IV is 6–7 times more stable than di-tert-butyl peroxide.

However, as is seen from Fig. 2, the organosilicon diperoxides themselves differ very substantially in thermal stability depending on their structure, i.e., on the nature of the alkyl radicals both at the silicon atom and at the peroxide group. Thus, diperoxides with a tert-butyl radical at the peroxide group are more stable than those with a tert-amyl radical. And depending on the radicals at the silicon atom, an alternating effect is observed, i.e., diperoxides with propyl and methyl radicals are more stable and those with an ethyl radical are the least stable. Thus, the alkyl radicals at the silicon atom increase the stability of the diperoxides in proportion to their positive inductive effect on the silicon atom: ethyl < methyl < propyl.

The diperoxide with an allyl radical at the silicon atom, IX (see Fig. 1), proved to be the least stable among the diperoxides studied. Evidently, the decrease in the thermal stability of this diperoxide is associated with the negative inductive effect of the allyl radical on the silicon atom, just as negative substituents reduce the stability of organic peroxide compounds (18–20).

It should be noted that the thermal decomposition of the diperoxide with the allyl radical, IX, does not follow the equation for monomolecular reactions, in contrast to the monoperoxides. In this case as well, the reasons for the deviation from monomolecular decomposition are not clear.

Trip-tert-butyl peroxyvinylsilane (X), as can be seen from Fig. 2 and Table 1, proved to be less stable in comparison with the diperoxides. Consequently, with the accumulation of peroxide groups at the silicon atom in the transition from mono- to di- and triperoxides, the thermal stability of silicon-organic peroxides decreases. Evidently, this is connected with an increase in the electronegativity of the silicon atom under the influence of the peroxide groups.

The data presented on the thermal decomposition of unsaturated organosilicon peroxides make it possible to use them more rationally in processes of high-temperature polymerization, as well as vulcanization, for which the authors of the present work propose their use (21).

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