

## THERMAL DECOMPOSITION OF THE COPOLYMER STYRENE-OXYGEN

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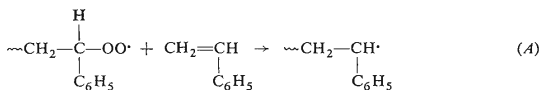
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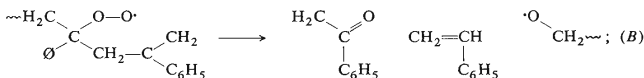
The rate of decomposition of polystyrene peroxide in toluene solution at 75°–110°C has been determined. The activation energy value thus found ( $E$  17.5 kcal/mol) indicates a considerable participation of induced decomposition in the process. The contribution of primary initiation was determined from the rate of polymerization of styrene initiated with polyperoxide (activation energy  $E$  33.1 kcal/mol). To explain the difference between the rate of total decomposition and the rate of primary initiation, a cyclic mechanism of reaction of oxyl or peroxy radicals with their own chain has been suggested, based on the known decomposition products.

The primary autoxidation initiation reaction belongs to the least investigated problems of the oxidation mechanism, in spite of the fact that it is of great importance both from the viewpoint of the autoxidation itself and from the viewpoint of investigation of the antioxidation stabilizers. The autoxidation of styrene in the absence of radical initiators exhibits a considerable autoacceleration effect. It is not known from the literature to what extent the copolymer of styrene and oxygen contributes to the total oxidation initiation in the first stages of oxidation. A number of authors agree that the first oxidation step consists in the formation of an adduct of styrene with oxygen; this adduct is very unstable and decomposes with formation of radicals capable of starting a chain reaction<sup>1,2</sup>. Copolymerization of styrene with oxygen and decomposition of the copolymer take place parallel to the formation of the adduct while yielding aldehydes; the radicals formed in the decomposition of the copolymer can again initiate the oxidation process.

Most of the data on the reactions of polystyrene peroxide are summarized in papers by Miller and Mayo<sup>3,4</sup>. In the oxidation of styrene under a sufficient pressure of oxygen a polyperoxide, *i.e.* styrene-oxygen copolymer, is formed in a ratio close to 1 : 1. At the same time, benzaldehyde, formaldehyde, and certain amounts of  $\alpha$ -hydroxyacetophenone,  $\alpha,\beta$ -epoxystyrene, and phenylethylene glycol are formed as the main products of decomposition. The activation energy of the formation of aldehydes is higher by approximately 6 to 10 kcal/mol than that of the reaction between styrene radicals and oxygen. Howard and Ingold<sup>4</sup> determined, by means of the rotating sectors method, the rate of the propagation reaction



and the rate constant of the square termination of the peroxy radicals; the order of magnitude of this constant is  $10^7$  ( $\text{mol l}^{-1} \text{s}^{-1}$ ), the corresponding activation energy being 1.8 kcal/mol. Moreover, they found that the termination reaction of peroxy radicals of the first order must also take place; its rate constant at  $40^\circ\text{C}$  is  $0.3 \text{ s}^{-1}$  (activation energy  $E$  11.6 kcal/mol). The value of this rate constant remains unaffected by the reaction between the peroxy radical and the styrene molecule or polyperoxide; it has been demonstrated, on the basis of the oxidation of  $\alpha$ -deuteriated styrene, that the termination of the first order occurs *via* elimination of the  $\alpha$ -hydrogen (with formation of ketone and  $\text{HO}\cdot$  radical which can either initiate a new chain, or be added to the aromatic ring with formation of the cyclohexadienone structure; after reaction with another peroxy radical, phenol is obtained which can further participate in the reaction<sup>5</sup>). Abadie and Marchal<sup>6</sup> assume that in the radiation degradation of polystyrene in the presence of oxygen, benzaldehyde and  $\alpha,\beta$ -epoxystyrene are formed by a cyclic mechanism



monomeric styrene is released in the process.

The rate of decomposition of the styrene-oxygen copolymer (1 : 1) was investigated in a preliminary manner only<sup>3</sup>: the thermal decomposition of polyperoxide alone and in benzene solution proceeds virtually at the same rate and approximately corresponds to a first order reaction; the presence of radical scavengers (styrene,  $\alpha$ -methylstyrene, hydroquinone) leads to a decrease in the decomposition rate. An investigation of the photolysis of polyperoxide in styrene revealed that no aldehydes were formed<sup>4</sup>, and reaction gave rise to a polymer containing residues of polystyreneperoxy chains. It is justified to assume, therefore, that the degradation of the polyperoxide chains to aldehydes proceeds by a mechanism differing from that of the primary initiation. An important part of the primarily formed radicals is deactivated by reaction with the scavenger while yielding products unable to initiate a new chain decomposition, thus slowing down the total rate of decomposition. In the primary initiation, an important part can be played by the end groups of polyperoxides, one third of which is known to consist of aldehyde and hydroxyl groups, the other two thirds probably containing hydroperoxides<sup>3</sup>. In the present work, an attempt has been made to determine the rate of decomposition of polystyrene peroxide and the amount of primary radicals initiating the chain decomposition of polyperoxide.

## EXPERIMENTAL

**Chemicals.** Styrene (Kaučuk, Kralupy) was freed from inhibitors by shaking with an alkali solution, dried and distilled,  $n_D^{20}$  1.5439; purity check by GLC. Methanol, benzene and tetramethylammonium chloride were of anal. purity grade; the solvents were distilled, and the purity was determined refractometrically and by GLC. The copolymer styrene-oxygen was prepared according to ref.<sup>3</sup> by oxidation of styrene at 45°C in the presence of  $\alpha, \alpha'$ -azo-bis-isobutyronitrile (further AIBN) with oxygen under a pressure of 760 Torr (500 ml of freshly distilled styrene was oxidized 24 h). After evaporation of half the volume of styrene at room temperature and reduced pressure the reaction mixture was precipitated by pouring into methanol. The product was reprecipitated by precipitation from benzene; 65 g of dry polyperoxide was obtained. The infrared spectrum (Fig. 1, measured with a Perking-Elmer 457 apparatus): 1708 (benzaldehyde carbonyl), 3400 (hydrogen bond between HO— and oxygen)<sup>7</sup>, 3540–3560 (hydroperoxide HO-groups)<sup>8</sup> and 3610, 3650 and 3700  $\text{cm}^{-1}$  (HO-groups); epoxide groups (811, 869 and 1256  $\text{cm}^{-1}$ ) were not detected. The molecular weight  $2870 \pm 5\%$  was determined ebulliometrically (degree of polymerization 20–22). For poly- 50 : 50 (styrene-co-oxygen), calculated: 70.59% C, 5.92% H; found: 70.73% C, 6.07% H.

**Determination of the  $\text{O}_2$  content in polyperoxide.** The usual method for iodometric determination of peroxides does not give reliable results in the case of the copolymer styrene-oxygen<sup>9,10</sup>. Its special modification is also unreliable<sup>3</sup>. Similarly, methods based on the oxidation of thiocresol<sup>4</sup> and oxidation of leucobase of the methylene blue<sup>11,12</sup> yield oxygen content values in the copolymer lower than the actual ones. For these reasons, a polarographic determination of oxygen<sup>13</sup> in the copolymer has been suggested. A number of electrolytes recommended for the polarography of organic peroxides<sup>14–16</sup> proved to be unsuitable because of the low solubility of polystyrene peroxide. We used a 0.156 molar solution of tetramethylammonium chloride in a mixture benzene-methanol (10 : 3). The polarographic determinations were carried out in a cell for non-aqueous media with a mercury bottom<sup>17</sup> using an LP 55 polarograph having an output adjusted for an EZ2 recorder, and also an LP 60 polarograph. The constants of the drop electrode: height of the reservoir 40 cm, drop time 1.9 s, outflow velocity of mercury 3.8 mg/s. When reduced at the drop electrode, polyperoxide yields one wave having the half-wave

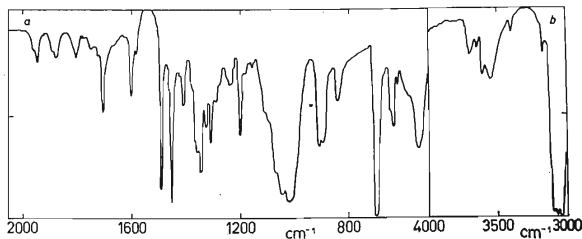


FIG. 1

Infrared Spectrum of Polyperoxide in Tetrachloromethane Solution  
Concentration *a* 13 wt. %, cell 0.251 cm; *b* 14.94 g/l, cell 10 mm.

potential  $-0.5-0.7$  V and another two waves with the potentials  $-1.55$  and  $-1.9$  V, corresponding to benzaldehyde and formaldehyde, respectively (during the investigation of the rate of decomposition of polyperoxide both waves increase proportionally to the degree of decomposition of the peroxide). At concentrations higher than  $5 \cdot 10^{-3}$  mol/l of polyperoxide the polarographic curves exhibit a maximum; at lower concentrations the diffusion current after reduction of peroxide is constant. The wave height was proportional to the square root from the height of the reservoir. The rate of decomposition of polyperoxide was determined so that samples of the reaction mixture, 0.1 to 1 ml in volume, were added to 10 ml of the electrolyte in the polarographic cell, and a stream of nitrogen was bubbled through the solution for 15 min. In the case of a quantitative determination of peroxide the wave height was taken as the mean from the determinations.

We compared the ratio of the limit current of polystyrene peroxide with tert-butyl hydroperoxide (Table I). The ratio of the values wave height/peroxide conc. for polyperoxide and tert-butyl hydroperoxide is  $c = 0.161$ . This fraction is considerably lower than that determined by Bovey and Kolthoff<sup>13</sup> ( $c = 0.395$ ) for polyperoxide prepared in the emulsion polymerization of styrene initiated with potassium persulphate, and for tert-butyl hydroperoxide. The low value is probably due to the considerable difference between the values of the diffusion coefficient of tert-butyl peroxide and polyperoxide. The difference between the value determined here and the value published in ref.<sup>13</sup> may be caused by the difference in the molecular weights of polyperoxides prepared by different procedures, and also by the different diffusion coefficients in the media used.

*Determination of the decomposition rate of polyperoxide.* The rate of decomposition of polystyrene peroxide was determined in a toluene solution at a constant initial concentration of 1 g polyperoxide in 100 ml of solution. The solution was freed from the dissolved gases by repeated freezing and evacuation under a pressure less than 0.1 Torr, by using the common procedure in a cylindrical vessel with sealed-on ampoules. After the last freezing the vessel was evacuated and closed. The contents were melted, and the solution was poured into the ampoules, which were then separated from the main vessel. The ampoules were inserted into a thermostat and after certain time intervals removed and analyzed. For comparison, some tests were also carried out in a vessel provided with a reflux. The polymer solution was bubbled with a stream of purified

TABLE I

Dependence Between the Concentrations of Tert-butyl Hydroperoxide and Polystyrene-co-oxygen for a Given Wave Height ( $h$ )

$h^b$ mm	Polyperoxide		t-Butyl hydroperoxide
	g/l	$10^{-3}$ mol/l <sup>a</sup>	$10^{-4}$ mol/l <sup>a</sup>
32	0.0805	5.90	0.953
64	0.1611	11.82	1.915
96	0.2416	17.73	2.86
135	0.3221	23.65	4.02

<sup>a</sup> Molar concentration of polyperoxide is given in the units styrene-oxygen  $\text{CH}_2-\text{CH}-\text{OO}-$ ;

<sup>b</sup> Wave height at sensitivity 1 : 70 mm.

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nitrogen for 10 min before placing into the thermostat. The samples were removed by means of a syringe under an overpressure of nitrogen after given time intervals. Both methods gave identical results.

*Determination of the rate of polymerization of styrene.* Polyperoxide was dissolved in an adequate amount of pure styrene and weighed into dilatometric ampoules with a stream of purified nitrogen. The rate of polymerization was measured with an automatic dilatometric apparatus<sup>18</sup>. The rate of thermal polymerization was followed in a similar manner.

## RESULTS AND DISCUSSION

### *Determination of the Rate of Decomposition of Polyperoxide*

The time dependence of  $\log P/P_0$  ( $P$  is the conc. of peroxide in mol/l at a time  $t$  min,  $P_0$  is the initial concentration of peroxide) over the initial period (Fig. 2) is virtually linear for temperatures lower than 100°C; within longer time intervals the decomposition is slowed down. The peroxide loss is controlled by the equation

$$k_d = 1.2 \cdot 10^{14} \exp(-17500/RT). \quad (1)$$

FIG. 2  
Decomposition of Polyperoxide in Toluene Solution  
Concentration of the polymer (mol/l):  
 $P_0$  initial,  $P$  at a time  $t$ .

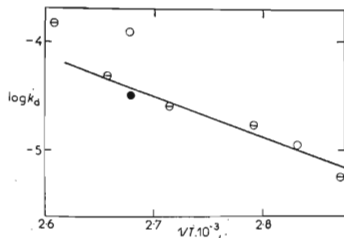
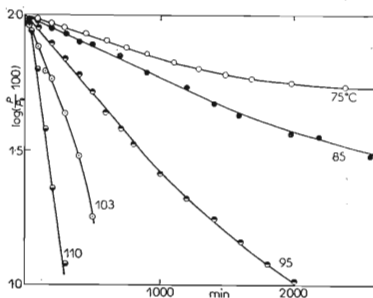


FIG. 3  
Dependence of the Rate Constant of Polyperoxide Decomposition on Temperature  
Calculated from:  $\ominus$  experimental data,  $\circ$  data in ref.<sup>4</sup> for decomposition in benzene,  $\bullet$  data of ref.<sup>4</sup> for decomposition in  $\alpha$ -methylstyrene.

The first order of reaction established here is in agreement with Mayo's and Miller's<sup>4</sup> observations acquired by the investigation of the decomposition of polyperoxide in benzene solution at 80° and 100°C: the rate constant  $k_d$  for decomposition in benzene solution at 80°C satisfies Eq. (1). Also for decompositions carried out at 100°C the agreement was within an order of magnitude; the difference between the rate constants (Fig. 3) is probably due to a departure from the linear dependence of  $\log P/P_0$  on time.

The activation energy determined here,  $E$  17.5 kcal/mol, is substantially less than the activation energy of the thermal decomposition of hydroperoxides and dialkyl peroxides (25–40 kcal/mol)<sup>1</sup>. The low value of activation energy indicates that the induced decomposition must play an important role in the total reaction mechanism.  $\alpha$ -Methylstyrene is a very good scavenger of the alkoxy and peroxy radicals; it is not capable of attacking the polyperoxidic chain<sup>5</sup>. If the value of  $k_d$  calculated from the data in refs<sup>3,4</sup> for the decomposition in  $\alpha$ -methylstyrene corresponds to the rate constants  $k_d$  of the decomposition in toluene solutions at lower temperatures (Fig. 3), it can be said that the number of radicals formed during the decomposition of the C—O—O—C bond and able to initiate a further decomposition is comparatively small. Hence, if the low activation energy of decomposition is taken into account, then the majority of C—O• produced by thermal decomposition must be deactivated in some other way. This is possible only by a reaction with their own chain, since termination by combination of two alkoxy radicals yields again the original peroxide, while termination by disproportionation gives rise to the aldehydic and hydroxyl end groups, without, however, releasing any detectable formaldehyde and benzaldehyde.

#### *Determination of the Rate of Initiation of Styrene Polymerization Initiated with Polyperoxide*

We have made an attempt to determine the portion of radicals capable of initiation after decomposition of the peroxidic bond. First, thermal polymerization of styrene without initiators was determined. The rate of initiation at 45, 60 and 70°C in the presence of polyperoxide was determined from the equation<sup>19</sup>

$$R_p = k_p k_t^{-1/2} M (k_i P)^{1/2} + R_t, \quad (2)$$

here,  $R_p$  is the rate of polymerization in  $\text{mol l}^{-1} \text{s}^{-1}$ ,  $M$  is the concentration of the monomer (mol/l),  $k_p$ ,  $k_t$ ,  $k_i$  are rate constants of propagation, termination and initiation of the styrene polymerization ( $\text{mol l}^{-1} \text{s}$ ), respectively, and  $R_t$  is the rate of thermal polymerization; the  $k_p/k_t^{1/2}$  values have been taken from a paper by Olivé and coworkers<sup>20</sup>. The results are summarized in Table II.

The dependence of the rate of polymerization at 45°C and 60°C on the square root from the peroxide concentration is linear within the limits of experimental error; a departure from the linear course was found at 70°C at higher peroxide concentrations. The decrease in the rate constant  $k_i$  with increasing polyperoxide concentration

is difficult to explain by mutual interaction of radicals with the adjacent polyperoxidic chain; it seems more likely that at higher temperatures there is an increase in the portion of the decomposition products capable of retarding the polymerization.

It follows from a comparison of the rate constants of the initiation with polyperoxide and of the decomposition of polyperoxide in toluene that the ratio  $k_i/k_d$  increases with increasing temperature (at 45°C 0.0076, at 60°C 0.0207, at 70°C 0.059). The activation energy calculated from the determined values of the rate constants  $k_i$  ( $E$  33.1 kcal/mol,  $A$   $3.5 \cdot 10^{14}$  s) corresponds to the activation energy needed for the thermal splitting of the O—O bond in dialkyl peroxides<sup>1</sup>. A considerable difference between the  $E_d$  and  $E_i$  values suggests that the splitting of the peroxide bond with formation of alkoxy radicals yields prevalingly radicals capable of the initiation reactions (combination with the styrene molecule or disproportionation by splitting-off of the hydrogen atom). Both reactions lead to a styryl radical which in the presence of oxygen yields a peroxy radical, or in the absence of oxygen reacts with the styrene molecules, thus initiating the polymerization chain. Besides, there must exist another mechanism requiring half the activation energy of the thermal splitting of the O—O bond. This parallel reaction is initiated with the styryloxy radical of the styrene unit or with a radical formed by splitting-off of the hydrogen atom from the hydroperoxidic group or of the tertiary hydrogen atom  $\sim\text{O}-\text{CH}(\text{Ph})-\text{C}-$

TABLE II

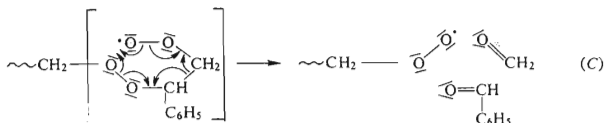
Dependence of the Velocity of Styrene Polymerization on the Concentration of Polystyrene-oxygen

Polyperoxide				Polyperoxide			
$\text{g l}^{-1}$	$\text{mol}^{1/2} \text{l}^{-1/2}$	$R_p \cdot 10^6$ $\text{mol l}^{-1} \text{s}^{-1}$	$k_i, 10^{-8} \text{s}^{-1}$ ( $k_d, 10^{-8} \text{s}^{-1}$ ) <sup>a</sup>	$\text{g l}^{-1}$	$\text{mol}^{1/2} \text{l}^{-1/2}$	$R_p \cdot 10^6$ $\text{mol l}^{-1} \text{s}^{-1}$	$k_i, 10^{-8} \text{s}^{-1}$ ( $k_d, 10^{-8} \text{s}^{-1}$ ) <sup>a</sup>
45°C				5.89	0.208	9.38	
—	—	0.76	0.582	6.53	0.219	12.52	
4.40	0.179	2.96	(76.7)	9.02	0.257	11.33	
8.50 <sup>B</sup>	0.249	3.94					
8.51	0.250	3.96					
9.12	0.260	3.65					
13.50	0.315	4.61					
60°C							
—	—	2.35	5.35			6.02	28.95
2.05	0.122	6.35	(258)	2.42	0.133	8.47	(490)
2.09	0.124	6.14		3.35	0.157	12.2	
4.36	0.179	8.53		5.02	0.192	17.34	
				6.42	0.217	20.35	
				13.1	0.311	24.50	

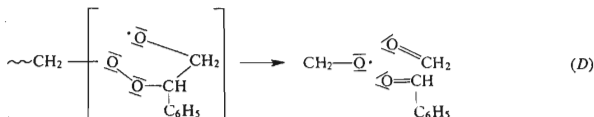
<sup>a</sup> Counted from Arrhenius' equation.

(R—O• or HO• radical).

The mechanism of this transformation is not known. The photolysis of polyperoxide in the presence of the radical scavengers yields a minimum amount of aldehydes<sup>4</sup>. This finding is at variance with the assumption that the decomposition should occur *via* some kind of zip mechanism along the chain. We assume that the decomposition into aldehydes occurs by an interaction of the styryloxy and styrylperoxy radicals with their own chain while regenerating the oxyl or peroxy radical. The peroxy radical in the transitional state can form a six-membered ring:



which undergoes decomposition with regeneration of the radical and formation of benzaldehyde and formaldehyde. Similarly, in the case of the oxyl radical a five-membered ring can arise:



The formation of both the five- and six-membered ring in the transitional state corresponds to the low activation energy of decomposition determined here ( $E_a = 17.5$  kcal/mol). The same activation energy (17 kcal/mol) was calculated for the formation of the six-membered ring in the case of the splitting-off of the secondary hydrogen atom by the action of the peroxy radical; for the tertiary hydrogen atom, a lower energy,  $E$  14 kcal/mol, was found. (The five-membered ring-secondary hydrogen atom,  $E$  11 kcal/mol; tertiary hydrogen atom,  $E$  8 kcal/mol<sup>21</sup>.)

If we assumed that in the case of polyperoxide the tertiary hydrogen atom was split off either from the proper (3–4-membered ring) or from the adjacent molecule of styrene (7–8-membered ring), then this reaction ought to have as its necessary consequence an instantaneous isomerization of the C• radical formed and a rearrangement of the hydrogen atom, since any other way would hardly lead to benzaldehyde and formaldehyde, which are the main products of decomposition. Moreover, the 3,4,7 and 8-membered rings are not energetically advantageous. The side products of decomposition, such as  $\alpha$ -hydroxyacetophenone, epoxide, *etc.*, can easily be pro-



duced by the side reactions or by the square termination of the oxy radicals. The six-membered ring of peroxy radicals is an analogue of Russell's mechanism of termination of the peroxy radicals, while the five-membered ring resembles molozonides which are transitionally formed in the reaction of ozone with the double bond. It is probable that the decomposition into aldehydes is a very fast process, and that no stabilization of molozonide and its rearrangement into ozonide takes place.

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