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FTD-ID(RS)T-0100-90

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RADICAL POLYMERIZATION OF DIENE HYDROCARBONS IN A PRESENCE OF PEROXIDE OF HYDROGEN AND SOLVENT

1. Effectiveness of initiation and rate of expansion H_2O_2 during oligomerization in metallic equipment

by

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PARTIALLY EDITED MACHINE TRANSLATION

FTD-ID(RS)T-0100-90 10 April 1990

MICROFICHE NR: FTD-90-C-000398

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English pages: 14

Source: Sintez i Fiziko-Khimiya Polimerov, Nr. 6, 1970, pp. 16-20

Country of origin: USSR
This document is a machine translation.
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К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
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М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere.
When written as ё in Russian, transliterate as yё or ё.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	$\sinh^{-1}$
cos	cos	ch	cosh	arc ch	$\cosh^{-1}$
tg	tan	th	tanh	arc th	$\tanh^{-1}$
ctg	cot	cth	coth	arc cth	$\coth^{-1}$
sec	sec	sch	sech	arc sch	sech^{-1}
cosec	csc	csch	csch	arc csch	csch^{-1}

Russian	English
rot	curl
lg	log

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RADICAL POLYMERIZATION OF DIENE HYDROCARBONS IN A PRESENCE OF PEROXIDE OF HYDROGEN AND SOLVENT.

1. Effectiveness of initiation and rate of expansion H_2O_2 during oligomerization in metallic equipment.

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Interest in oligomers of diene and vinyl series with terminal reactive groups increased in recent years. In particular, are of interest diene oligomers with the terminal hydroxyl groups as basis for obtaining polyurethanes. At present in the USA and Japan are produced on the experimental production scale the oligomers of butadiene, which have at the ends of the hydrocarbon chain the hydroxyl groups. These are liquid oligobutadienes of brand R-15M and R-45M (firm "Sinclair Retgochemical Suc."/USA) → Russian translation [illegible] [5, 6, 10] and hydroxyl-containing oligobutadienes "Nisso PB" series σ, produced by firm "Nippon Soda" (Japan) [7]. Polyurethanes, obtained on the basis of the oligomers indicated, in contrast to those obtained on the basis of simple and polyesters, possess number of valuable properties - low temperature of vitrification (to -80°C), excellent adhesion to different materials, excellent hydrolytic stability. These oligomers can be obtained both on the free radical and by the ionic mechanism. Most promising, in view of simplicity and cheapness, is considered the method of the radical polymerization of diene hydrocarbons in the presence of peroxide of hydrogen and methanol, proposed recently in IKhVS of AS UkSSR Yu. L. Spirin with coworkers [3]. Initiators of polimerization in this method are the hydroxyl radicals, which are generated during the homolytic decomposition of peroxide of hydrogen PDO by the effect of elevated temperatures (80-100°C). Being located in the medium of monomer, the resultant radicals initiate a chain growth, bringing in the final analysis to obtaining of oligomers with the terminal hydroxyl groups.

Kinetic data on oligomerization of isoprene in presence H_2O_2 were obtained by authors of this method while conducting of process in glass [2]. It is known that the rate of expansion H_2O_2 depends on material and character of the surface of reaction vessel [4]. Since kinetics of the process of the oligomerization of dienes is connected with expansion H_2O_2, it is possible to assume that upon transfer from the glass to the metallic equipment the material of reactor has the specific effect on the process of oligomerization. For this purpose macrokinetics of the process of the oligomerization of isoprene and butadiene was studied by us and the questions, connected with some special features of the decomposition of hydrogen peroxide in the metallic equipment, were investigated.

Discussion of results.

Fig. 1 gives kinetic curves of formation of isoprene oligomer with different ratios of isoprene and H_2O_2. Dotted curve reflects oligomerization in the glass (data of IKhVS).

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As can be seen from Fig. 1, the rate of formation of oligomer in the glass, other conditions being equal, is lower than in the metallic equipment. This is explained by a difference in the rate constants of expansion H_2O_2 in the glass and the metal (stainless steel Kh18N9T). The rate constant of expansion H_2O_2 in the metal under the described conditions it is equal to

$$K_{р.з.} = 24 \cdot 10^{10} \exp\left(-\frac{24900}{RT}\right) \overset{(1)}{сек^{-1}}.$$

Key: (1). s^{-1}.

Here one should indicate one special feature, which concerns rate of expansion H_2O_2 in metal. Despite the fact that the reactor of oligomerization was thoroughly passivated, but to the measure for conducting experiments in it the rate of expansion H_2O_2 from one experiment to the next was decreased, which, apparently, is connected with the continuous passivation of the surface of reactor (Fig. 2).

Fact indicated can introduce some corrections into value of pre-exponent $K_{р.з.}$ However, energy of the activation of expansion H_2O_2 $E_{акт.}$ equal to 24.9 kcal/mole, in this case it will not be changed, since it is determined from experiments, carried out into the short time interval.

Fig. 3 gives kinetic curves of consumption of isoprene and expansion H_2O_2. According to these curves can be determined the rate of polymerization $V_п$ and velocity of initiation $V_{ин} = V_{расп} f$, where f - coefficient of the effectiveness of initiation.

For stationary process rate of polymerization

$$V_п = V_{ин}^{1/2} \frac{K_p}{\sqrt{K_o}} [M].$$

For t=3 hour

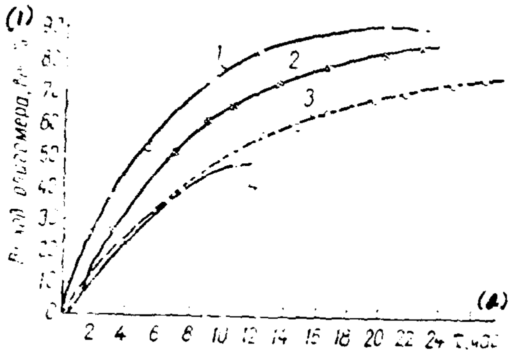
$$V_п = 6,75 \cdot 10^{-5} \text{ моль/л·сек } (1)$$
$$V_{расп} = 1,19 \cdot 10^{-5} \text{ моль/л·сек;}$$
$$[M] = 3,05 \text{ моль/л } (2)$$

Key: (1). mole/l·sec. (2). mole/l.

Separately carried out balance experiment determined value f=0.2. Then

$$\frac{K_p}{\sqrt{K_o}} = \frac{V_п}{V_{ин}^{1/2}[M]} = \frac{6,75 \cdot 10^{-5}}{\sqrt{1,19 \cdot 10^{-5} \cdot 0,2} \cdot 3,05} = 1,42 \cdot 10^{-2} \text{ (моль/л·сек)}^{1/2} \ (1).$$

Key: (1). (mole/l·sec) 1/2.



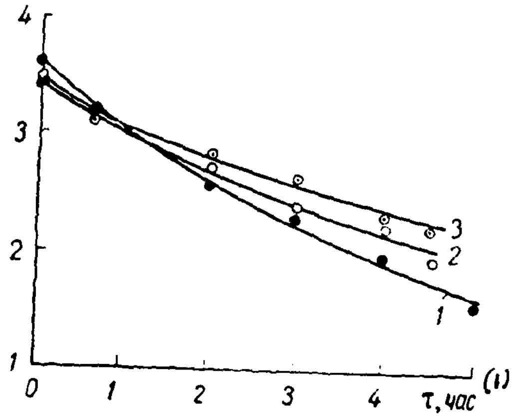


Fig. 1. Fig. 2.

Fig. 1. Dependence of yield of oligomer in time with different ratios of isoprene (H_2O_2, t=90°C): 1 - 3:1; 2 - 5.4:1; 3 - 3:1; 4 - 14.4:1.

Key: (1). yield of oligomer, wt.%. (2). hour.

Fig. 2. Dependence of rate of decomposition of hydrogen peroxide on time: 1 - experiment 31 (total operating time of autoclave 200 hour); 2 - experiment 53 (350 hour); 3 - experiment 73 (470 hour).

Key: (1). hour.

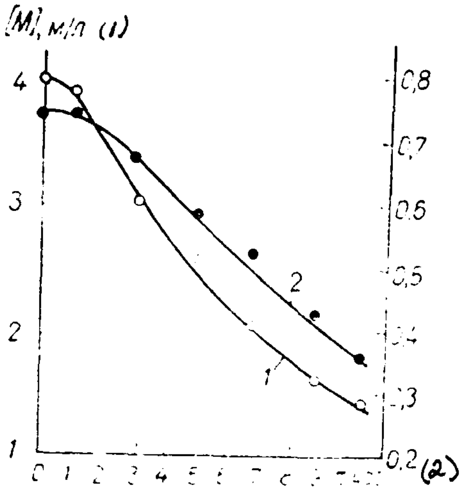


Fig. 3. Dependence of consumption of isoprene (1) and decomposition of peroxide of hydrogen (2) on time, t=90°C.

Key: (1). m/l. (2). hour.

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Obtained value $\frac{K_p}{\sqrt{K_0^{1/2}}}$, which is the important characteristic of polymerizing process, differs little from value $\frac{K_p}{K_0^{1/2}}$ determined for the oligomerization in glass [2].

From ratio of velocities of polymerization and initiation average/mean degree of polymerization [1]

$$\bar{P} = \frac{V_{\text{п}}}{V_{\text{ин}}}.$$

can be determined For experiment given above

$$P = \frac{6{,}75 \cdot 10^{-5}}{1{,}19 \cdot 10^{-5} \cdot 0{,}2} = 28{,}3; \quad \bar{M} = 28{,}3 \cdot 68 = 1920,$$

where 68 - molecular weight of elementary link. Molecular weight, determined ebullioscopically, is equal to 2380, which satisfies computed value.

We assume in examination of mechanism of oligomerization for simplicity that H_2O_2 is separated into two hydroxyl radicals according to equation $H_2O_2 \xrightarrow{rc} 2HO$. Undoubtedly, this concept is very simplified. In actuality the mechanism of expansion H_2O_2 is very complex. Radicals OH can be formed, also, according to another diagram. In particular, many researchers at present are inclined to the electrochemical mechanism of expansion H_2O_2 [8]:

$$
\begin{gathered}
H_2O_2 + l \rightleftarrows OH^{\cdot} + OH^{1};\\
OH^{\cdot} + l \rightarrow OH^{1};\\
H_2O_2 - l \rightleftarrows H^{+} + HOO^{\cdot};\\
HOO^{\cdot} - l \rightarrow H^{+} + O_2.
\end{gathered}
$$

Furthermore, H_2O_2 is subjected to the induced decomposition:

$$
\begin{gathered}
OH^{\cdot} + H_2O_2 \rightarrow HOO^{\cdot} + H_2O;\\
HOO^{\cdot} + H_2O_2 \rightarrow H_2O + O_2 + OH^{\cdot}.
\end{gathered}
$$

Collaboration of hydroxyl radicals, which go directly to initiation of polymerization, characterizes value of effectiveness of initiation f. This coefficient enters into the kinetic equation of velocity of initiation $V_{\text{ин}} = 2K_{\text{разл}}f\,[H_2O_2]$ and serves as if measure of the selectiveness of the decomposition of initiator. Usually in the radical reactions f=0.6-0.7 [1].

Table 1. Effectiveness of peroxide initiation of hydrogen during the oligomerization of isoprene and divinyl in the medium of methanol [1].

(1) Номер опыта	(2) Мономер	(3) Содержание метанола, % вес.	f	(4) Примечание
22	(5) Изопрен	58.4	0,19	
69	Бутадиен (6)	40,0	0,30	(7) При перемешивании со стружкой Х18Н10Т
70	Изопрен ⑤	58.4	0,22	
72	Бутадиен ⑥	46.0	0.32	
74	»	60.0	0.26	
75	»	60.0	0.27	(8) При перемешивании
82	Изопрен ⑤	58.4	0.26	
[illegible]	»	58.4	0.22	
[illegible]	»	40.0	0.24	
[illegible]	»	40.0	0.24	

Key: (1). Number of experiment. (2). Monomer. (3). Content of methanol wt.%. (4). Note. (5). Isoprene. (6). Butadiene. (7). During mixing with shaving Kh18N10T. (8). During mixing.

FOOTNOTE [1]. Temperature in experiment for isoprene of 90°C, for remaining monomers of 100°C. ENDFOOTNOTE.

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In case of f=0.2-0.3 (Table. 1) in question. The low value f, found by us, is somewhat unexpected, since there is a significant excess of monomer relative to H_2O_2. This can be explained as follows. First, during calculation f it was assumed that each molecule H_2O_2 generates two hydroxyl radicals, i.e., is separated according to diagram $H_2O_2 \rightarrow 2HO$. If we for calculation take the equations of the electrochemical mechanism, where one molecule H_2O_2 gives one OH-radical, then value f will be two times higher. The presence of a large quantity of solvent can be another reason for the low effectiveness of initiation.

One should stop especially on role of solvent in this process. Table 2 gives the data, which concern the rate constant of expansion H_2O_2, which grows in proportion to the decrease of the content of methanol. Are interesting also the data about the effect of mixing reaction mass.

In Table. 3 are brought results of experiments, carried out without mixing and with mixing and differing, furthermore, by different content of solvent in reaction mixture. As can be seen from data of Table 3, the rate of expansion H_2O_2 during the mixing strongly increases. Kinetic data, given in Tables 2 and 3, testify in favor of the so-called cell effect. Usually "cell effect" is called the recombination of radicals in the micro-space, limited "cell", impeding the diffusion of radicals from it and contributing thus to the course of the reactions of the induced decomposition H_2O_2. In the presence of "cell effect" due to the recombination of radicals must be decreased the rate of expansion H_2O_2. moreover the greater the concentration of solvent, the more noticeable must be effect. This regularity (see Table 2) with an increase in the content of methanol from 40 to 60% is decreased almost two times (experiments 61 and 73). During the mixing the contact of radicals with the monomer is improved, that also is developed in an increase in the rate of expansion H_2O_2. Difference K in the case of mixing must be smoothed in proportion to the decrease of the content of solvent.

This is observed in experiments, given in Table 3. Thus, with 60% of methanol during mixing K_p[illegible] 6.6 times more, and with 40% of methanol - altogether only 1.9 times more than in the case of the absence of mixing.

Although it is customary to assume that in radical reactions solvent does not have great effect on reaction however at stage of initiation (monomolecular decomposition H_2O_2), which is common chemical reaction, this effect can be significant.

Table 2. Rate constants of expansion H_2O_2 during the oligomerization of dienes, t=100°C.

(1) Номер опыта	(2) Мономер	(3) Содержание метанола в реакционной смеси, %	$k_{расп} \cdot 10^5$, $с^{-1}$ (4)
76	Изопрен (5)	60	3.34
73	»	60	2.75
59	Бутадиен (6)	66	3.62
54	Изопрен ⑤	43	5.0
61	»	40	5.6

Key: (1). Number of experiment. (2). Monomer. (3). content of methanol in reaction mixture, %. (4). s^{-1}. (5). Isoprene. (6). Butanediene.

Table 3. Effect of mixing and concentration of methanol on the rate of expansion H_2O_2 during the oligomerization of isoprene, t=100°C.

(1) Номер опыта	(2) Содержание метанола в реакционной смеси, %	$k_{расп} \cdot 10^5$, $с^{-1}$ (3)	(4) Примечание
73	60	2.75	Без перемешивания (5)
76	60	18.2	При перемешивании (6)
61	40	5.6	Без перемешивания ⑤
[illegible]	40	10.4	При перемешивании ⑥

Key: (1). Number of experiment. (2). Content of methanol in reaction mixture, %. (3). s^{-1}. (4). Note. (5). Without mixing. (6). During mixing.

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Nandi and Palit [9], studied the polymerization of methylmethacrylate in different solvents in presence H_2O_2, detected that the rate constant of initiation substantially is changed with a change in the concentration of solvent. The authors indicated explain this by the "effect of solvent".

Our data about effect of mixing on rate of expansion H_2O_2, apparently, cannot be explained by one "cell effect". Here should be taken into consideration contact H_2O_2 with the surface of the autoclave, whose intensity increases during the mixing. Since is shown [4] effect of surface on the rate of expansion H_2O_2, this fact so can be one of the reasons for an increase in the rate of expansion H_2O_2, during the mixing.

Experimental part.

Experiments were conducted in autoclave made of steel Kh18N10T with ratio of utilized volume to surface of V/S=1.17 cm.

Accuracy of thermostating ±1.5°C. While conducting of experiments with isoprene through the specific time intervals in the upper methanol layer was determined the content of that not reacted H_2O_2 and isoprene. Concentration H_2O_2 was determined by titration $Ce(SO_4)_2$, the concentration of isoprene - gas-chromatographically. A quantity of formed oligomer was calculated from the data of the gas-chromatographic analysis of unreacting isoprene in the methanol layer. The obtained concentration H_2O_2 in the methanol solution was recounted taking into account the formed oligomer to entire reaction mass. $K'_{\text{расп}}\,H_2O_2$ were calculated from the obtained values according to the first-order equation The gas-chromatographic analysis of isoprene was conducted on chromatograph UKh-1. As the inert carrier was used the diatomaceous brick INS-600, as immobile phase it served polyoxypropyleneglycol with molecular weight 2000 (of 20% weight of carrier), temperature of 65-67°C. During the oligomerization of butadiene concentration H_2O_2 in the methanol solution was determined after the blow-off of butadiene.

Value of coefficient of effectiveness of initiation f is found from balance experiments, in which was determined quantity of that decomposing H_2O_2 and quantity of hydroxyls in oligomer (among other things in oligomer, dissolved in methanol). The portion of hydroxyls, found in the oligomer, from the total number of that decomposing H_2O_2, and composes the coefficient of the effectiveness of initiation.

Conclusions.

1. Is studied kinetics of expansion H_2O_2 during oligomerization of isoprene and divinyl in metallic equipment. the effectiveness of peroxide initiation of hydrogen is determined. Under the conditions $f=0.2-0.3$ being investigated.

2. Effect of methanol on rate and effectiveness of initiation is established. Is assumed the presence of "cell effect" during the

oligomerization in this solvent.

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