Kinetic peculiarities of the reaction of liquefied hydrogen sulfide with propylene oxide

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The kinetics of the liquid-phase reaction of hydrogen sulfide with propylene oxide was studied. In the presence of excess epoxide, the reaction occurred in two successive macrostages: (1) formation of 2-hydroxypropane-1-thiol and (2) formation of 1,1'-di(2-hydroxypropyl) sulfide. Both of the stages are autocatalytic. 2-Hydroxypropane-1-thiol was mainly formed in the presence of excess H_2S . The overall third order of the reaction (the first with respect to each reagent and to 2-hydroxypropane-1-thiol) was found. A kinetic scheme was proposed, and the rate constants of particular stages were calculated. The influence of various catalysts (active carbon, ion-exchange resins, metal oxides, and others) was studied, and the relative efficiency of some of them was determined.

Key words: hydrogen sulfide, propylene oxide, catalysis, autocatalysis, kinetics, rate constants.

Early works¹⁻⁶ on the reactions of hydrogen sulfide with epoxy compounds were mainly preparative. In some of them, the effects of temperature, solvent, and catalytic additives on these reactions were studied. The kinetics of the reactions of H_2S with epoxy compounds was mainly studied using solvents that were not inert in these reactions.⁴⁻⁶

This work is devoted to studying the kinetics and mechanism of the previously found⁷ reaction of hydrogen sulfide with propylene oxide (PO). The process was carried out without a solvent at temperature and pressure that allow the reagents to exist in the liquified state. The occurrence of the reaction in the liquid phase in the absence of solvents makes it possible to study in more detail the kinetics and mechanism of the reaction and to observe all its peculiarities, including those that could not be observed in the presence of a solvent.

Experimental

The reaction of liquefied H_2S with PO was carried out in an autoclave-type reactor with a magnetic stirrer.⁸ Liquefied H_2S and PO were loaded into the reactor. The reaction was carried out in an inert gas (nitrogen) atmosphere at 75 °C and 75 atm. The moment of achievement of the needed temperature was taken as the beginning of reaction. Analysis of the critical temperatures and pressures of the reagents showed that the conditions of the reaction are determined by the critical parameters of hydrogen sulfide.^{9,10} A 2--3-mL sample for analysis was taken in a sampler, from which the liquid component moved to a measuring cell due to throttling, and the gas component moved to a gasometer. The liquid sample was analyzed for the content of PO and reaction products by GLC, and the content of H_2S was determined using the volumetry method (a saturated solution of $CuSO_4$ was used as the absorbent). Triethylamine, potassium hydrosulfide, alcohol solutions of sodium and potassium ethylates, anion-exchange resin AV-17-8, strongly basic anion-exchange resin IOS-3, cation-exchange resin KU-2, iron and lead oxides, active carbon (dry alkaline, finely dispersed), and bidistilled water were used as catalytic additives.

Results and Discussion

The reaction of hydrogen sulfide with PO occurs in two stages.

$$H_{2}S + H_{2}C-CH-CH_{3} \longrightarrow HSCH_{2}CH(CH_{3})OH (1)$$

$$HSCH_{2}CH(CH_{3})OH + H_{2}C-CH-CH_{3} \longrightarrow O$$

$$SICH_{2}CH(CH_{3})OH]_{2} (2)$$

A decrease in the reaction volume during the process is a specific feature of this reaction in the liquid phase in the absence of a solvent. Therefore, in several cases, in particular, to obtain the material balance of the system, a change in the amount (but not the concentration) of each component of the reaction mixture was calculated; to find inflection points, kinetic curves of consumption of the reagents and accumulation of the reaction products were plotted in "amount of substance (g-mol) time" coordinates.

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Time	H ₂ S	РО	НРТ	DHPS	Balanc	e (%)
/h	mol			for sulfur for		for PO
0	1.00	0.82	0	0	100	100
5.6	0.98	0.76	0.03	0	101	96.3
9.2	0.95	0.82	0.05	0	100	106
13.4	1.10	0.76	0.07	0	117	101.2
28.6	0.88	0.72	0.12	0	100	102.4
35.1	0.70	0.60	0.23	0	93	101
40.6	0.50	0.31	0.55	0	105	105
45.5	0.21	0	0.75	0.02	98	96
48.7	0.20	0	0.76	0.03	9 9	100

Table 1. Material balance with respect to sulfur-containing components and propylene oxide at $\sigma = 0.82$

Despite a complicated character of the system and certain difficulties in analysis of the components of the reaction mixture, the material balance with respect to sulfur-containing components and PO during the reaction can be considered as satisfactory (see Table 1). This also indicates the homogeneity of the reaction mixture, which should be expected because it is known that liquid H_2S is a good solvent for many organic compounds.¹⁰

The kinetic curves of consumption of PO and H_2S and accumulation of 2-hydroxypropane-1-thiol (HPT)



Fig. 1. Kinetic curves of consumption of PO (1) and H₂S (2) and curves of accumulation of HPT (3) and DHPS (4) for $\sigma = 1.88$ at 75 °C and 75 atm. N is the amount of compounds.



Fig. 2. Kinetic curves of consumption of H₂S (1) and PO (2) and curves of accumulation of HPT (3) and DHPS (4) for $\sigma = 0.82$ at 75 °C and 75 atm. N is the amount of compounds.

and 1,1'-di(2-hydroxypropyl) sulfide (DHPS) in the absence of catalytic additives (the molar ratio of PO to $H_2S \sigma = 1.88$) are presented in Fig. 1. As seen in Fig. 1, the reaction of H₂S with PO in the liquid phase is characterized by a slow period equal to 35-40 h during which the reagents are slowly consumed to form HPT (up to 0.18 mol). Then the reaction proceeds quite rapidly, and the maximum amount of thiol reaches 0.52 mol, i.e., hydrogen sulfide is transformed into HPT by 70%, and the latter is the only main final product of the reaction, which lasts 54 h. Then HPT, H₂S, and PO are consumed rapidly with quantitative formation of DHPS. At $\sigma = 1.88$, the reaction has a pronounced stepped character with two macrostages separated in time: the formation of HPT and formation of DHPS. Thiol is predominantly formed in the reaction of PO and H₂S taken in equivalent concentrations or in the presence of excess H₂S (Fig. 2). The kinetic curves of consumption of PO and H_2S and accumulation of HPT in the absence of catalytic amounts at $\sigma = 0.82$ are presented in Fig. 2. As can be seen in Fig. 2, after a period of slow reaction that lasts 20-25 h, the process accelerates and ceases after the complete consumption of PO, and unreacted hydrogen sulfide remains in an amount of 0.2 mol.

It has previously been $shown^{2,4,6}$ that 1,1'-di(2-hydroxyalkyl) sulfides accelerate both the first and second stages of the reaction of hydrogen sulfide with epoxy compounds. Similar data on a catalyzing effect of 2-hydroxyalkane-1-thiols are unknown. In this work, we observed an S-like character of the kinetic curves of



Fig. 3. Kinetic curves of consumption of $H_2S(l)$ and PO(2) and curve of accumulation of HPT (3) for $\sigma = 1.0$ at 75 °C and 75 atm. HPT (0.18 mol) was introduced at the beginning of the reaction. N is the amount of compounds.

accumulation of the reaction products, a high conversion of the starting reagent (up to 50%) at the inflection point (for $\sigma = 1.88$, the inflection point is within 45–50 h, and that for $\sigma = 0.82$ is in the 35–38 h range), and a high relative rate of formation of the reaction products inherent in this reaction (w is the ratio of the reaction rate at the inflection point to the rate at the initial stage of the reaction), which can be indicative of an autocatalytic process. However, direct evidence for the autocatalytic character of the process is the increase in its rate when the reaction product is introduced into the system: HPT for the first stage and DHPS for the second stage. The results of the experiment on the introduction of thiol into the reaction mixture containing H₂S and PO $(\sigma = 1)$ are presented in Fig. 3. Comparison of Figs. 2 and 3 shows that the introduction of HPT increases the rate of its accumulation by 2.5 times, and the reaction ceases at 8 h. The acceleration of the reaction observed in this case can be related to the catalytic effect of HPT only, because DHPS begins to accumulate 5 h after the beginning of the experiment (0.005 mol), when the reaction is virtually accomplished.

We also examined the accelerating effect of another thiol, 2-hydroxyethane-1-thiol, on the reaction of H_2S with PO. As seen in Fig. 4, the introduction of this thiol accelerates the process, and the reaction ceases after 17 h. In this case, HPT is accumulated without a noticeable consumption of 2-hydroxyethane-1-thiol added to the reaction mixture. Since PO was taken in a small excess over H_2S ($\sigma = 1.22$), 2-hydroxyethane-1-thiol (catalytic additive) is consumed at the final stage of the reaction along with the reaction product HPT (it performs autocatalysis) interacting with PO.

It follows from the data presented that the reaction of H_2S with PO occurs in a complex kinetic regime when both products accelerate the reaction.

To establish the order of the autocatalytic reaction at the first macrostage, we determined the amount of consumed reagent or product at the moment corresponding to the inflection point on the kinetic curve of



Fig. 4. Kinetic curves of consumption of PO (I), H₂S (2), and 2-hydroxyethane-1-thiol (4) introduced at the beginning of the reaction in an amount of 0.116 mol and curve of accumulation of HPT (3). N is the amount of compounds.

accumulation of the reaction product (see Fig. 2). Graphical analysis of the kinetic curve of HPT accumulation showed that the inflection point lies within the 35-38 h range at ~0.30-0.35 moles of accumulated thiol (or 0.30-0.35 moles of consumed H₂S). We found that at the inflection point $\xi_{inf} = x/A_0 = 1$ mol, where x is the increase in the amount of thiol or consumed H₂S in moles, and A_0 is the initial amount of H_2S , equal to 1 mol. Then we obtain that $\xi_{inf} = 0.9/3 - 1.05/3$. The found ratio of the amount of consumed substance to its initial amount at the inflection point is close to 1/3, which indicates the overall third order (the first order with respect to the reaction product and the second with respect to the reagents) and agrees with the data on the third order of reactions of this type (interaction of compounds containing the sulfhydryl group with epoxy compounds), for which the first order with respect to each initial component and the first order with respect to the reaction product have been determined.¹¹

The reaction of H_2S with PO that proceeds in two macrostages in the complex catalytic and autocatalytic regimes can quantitatively be described by the following kinetic scheme:

$$H_2S + PO \longrightarrow HPT$$
, (3)

$$H_2S + PO \xrightarrow{HPT} HPT,$$
 (4)

$$PO + HPT \longrightarrow DHPS,$$
 (5)

$$H_2S + PO \xrightarrow{DHPS} HPT,$$
 (6)

$$PO + HPT \quad DHPS \quad DHPS \quad (7)$$

The autocatalytic reaction develops in the presence of either minor amounts of the reaction product or a catalytic reagent in the stage of formation of this product or during the reaction resulting in its formation. In the first two cases, the concentration of this "primer" enters the reaction rate constant as a constant value.

For the first macrostage, the formation of HPT from H_2S and PO (reaction (3)) during catalysis of the reaction by metal oxides on the reactor surface can be this reaction. The HPT accumulated in this reaction results in the development of the autocatalytic process (4). Sulfide DHPS forms when HPT reacts with PO in reaction (5), similar to reaction (3) (catalytic effect of the reactor wall).

It follows from the experimental data that the product of the second stage of the reaction (DHPS) catalyzes the formation of HPT, which is shown by reaction (6). In addition, DHPS accumulated in reaction (5) results in the development of the autocatalytic process (reaction (7)).

Using the kinetic scheme (reactions (3)—(7)) and the separation of macrostages (1) and (2) in time, we determined the rate constants of autocatalytic reactions

of formation of mercaptane (1st macrostage) and sulfide (2nd macrostage). We also determined the dependence of the position of the inflection point ξ_{inf} on the kinetic curve of accumulation of mercaptan on the ratio of PO and H₂S concentrations.

The equation of autocatalysis for description of the 1st macrostage of the third-order reaction (4), taking into account reaction (3) (noncatalytic formation of mercaptan), can be written as follows:

$$d[HPT]/dt = k_4[H_2S][PO][HPT] + k_3[H_2S][PO].$$

Designating the increase in the concentration of the reaction product (HPT) by x and taking into account that this increase equals the decrease in H_2S and PO, we obtain the equation

$$dx/dt = k_4([H_2S]_0 - x)([PO]_0 - x)(k_3/k_4 + x).$$
(8)

If the HPT "seed" was introduced at the beginning of the reaction, $[HPT]_0$ appears in Eq. (8) instead of k_3/k_4 .

Introducing the dimensionless variables and parameters

we can transform Eq. (8) into the following form:

$$d\xi/d\tau = (1 - \xi)(\sigma - \xi)(\xi_0 - \xi).$$
(9)

The position of the inflection point is determined by the condition $d^2\xi/d^2\tau = 0$, from which at $\sigma = 1$ and low ξ_0 values $\xi_{inf} = 1/3$, *i.e.*, the inflection point is achieved when 1/3 of each of the reagents is consumed. When the reagents are not taken in equimolar amounts, *i.e.*, $\sigma \neq 1$, the position of the inflection point for the HPT reaction product does not correspond to 1/3 and is shifted toward 1/2 as σ increases. We found the dependence of the ξ_{inf} value at the inflection point of the kinetic curve of accumulation of 2-hydroxypropane-1-thiol on the ratio of PO and H₂S concentrations (σ):

The dependence of ξ_{inf} on the initial ratio of reagents was used to determine the needed correction to the order of the reaction of PO with H₂S at their ratio $\sigma = 1.88$.

Graphical analysis of the kinetic curve of HPT accumulation for $\sigma = 1.88$ (see Fig. 1) shows that the inflection point lies within the 45-50 h interval. As seen from the data in Table 1, at $\sigma = 1.88$ the inflection point corresponds to the time when not 1/3, but ~1.24/3, of the initial substance is consumed. The corresponding experimentally found value is ~1.38/3. The deviation of the experimental value from the calculated one is most likely related to the fact that the inflection point is attributed to the time when some amount of DHPS (0.02 mol) has already accumulated in the system, and this substance, being the catalyst of the first stage of the reaction, affects the position of the inflection point, shifting it toward achievement of a higher conversion.

Equation (9) describes the first macrostage of the autocatalytic reaction of H_2S with PO and can be used for the determination of the rate constant of this reaction. Then it can be written in the following form:

$$\tau = \frac{1}{(\xi_0 + 1)(1 - \sigma)} \ln(1 - \xi) + \frac{1}{(\xi_0 + \sigma)(1 - \sigma)} \ln \frac{\sigma}{\sigma - \xi} + \frac{1}{(\xi_0 + 1)(\xi_0 + \sigma)} \ln \frac{\xi_0 + \xi}{\xi_0}.$$
 (10)

From this, taking into account the values of dimensionless variables, we obtain

$$k_{4} = \frac{1}{0.43[H_{2}S]_{0}^{2}} \left[\frac{1}{(\xi_{0}+1)(1-\sigma)} \log(1-\xi) + \frac{1}{(\xi_{0}+\sigma)(1-\sigma)} \log \frac{\sigma}{\sigma-\xi} + \frac{1}{(\xi_{0}+1)(\xi_{0}+\sigma)} \log \frac{\xi_{0}+\xi}{\xi_{0}} \right]. (11)$$

For cases where ξ_0 is close to zero (*i.e.*, fulfillment of the condition $\xi_0 \ll 1$; $\xi_0 \ll \sigma$; $\xi_0 \ll \xi$), Eq. (11) can be simplified:

$$\frac{1}{1-\sigma}\log(1-\xi) - \frac{1}{\sigma(1-\sigma)}\log(\sigma-\xi) + \frac{1}{\sigma}\log\xi =$$
$$= \frac{1}{\sigma}\log\xi_0 - \frac{1}{\sigma(1-\sigma)}\log\sigma + 0.43k_4[H_2S]_0^2 \cdot t . (12)$$

Taking into account Eq. (12), the rate constant of the autocatalytic reaction and ξ_0 can be determined by the graphical method. Based on this, we obtain the dependence of θ on t

$$\theta = \frac{1}{1-\sigma}\log(1-\xi) - \frac{1}{\sigma(1-\sigma)}\log(\sigma-\xi) + \frac{1}{\sigma}\log\xi$$

We found the following values: $k = 2.1 \cdot 10^{-7}$ L² mol⁻² s⁻¹ and $\xi_0 = 2.7 \cdot 10^{-2}$ for $\sigma = 0.82$, $k_4 = 1.9 \cdot 10^{-7}$ L² mol⁻² s⁻¹ and $\xi_0 = 5.6 \cdot 10^{-2}$ for $\sigma = 1.88$. The use of Eq. (12) is limited because of the assumptions accepted. Although the ξ_0 values obtained are low, they are comparable with the ξ values for the initial moments, which reflects the accuracy of determination of the reaction rate constant. Therefore, the value obtained for the rate constant of the autocatalytic reaction is approximate and will be refined further.

Based on the data in Fig. 1 and Eq. (12), we estimated the k_7 rate constant of the autocatalytic reaction of PO with HPT under the assumption that reaction (2) is characterized by the same regularities as reaction (1), and Eq. (12) can be applied for reaction (2) as well. In the calculation of the rate constant, the beginning of this reaction was referred to the maximum HPT concentration, equal to 4.6 mol L^{-1} , at concentrations of PO and DHPS equal to 7.15 and 0.27 mol L⁻¹, respectively. The account begins from the moment t = 53.2 h accepted as the beginning of reaction (2). For this reaction, $\sigma = [PO]/[HPT] = 1/55$. We found that $k_7 = 1.2 \cdot 10^{-6}$ L² mol⁻² s⁻¹. Since as DHPS forms in reaction (2), HPT continues to accumulate due to the unreacted H₂S in reaction (1), the rate constant obtained should be refined.

Quantitative examination of autocatalytic reactions on the basis of Eqs. (10)-(12) is most substantiated when one such stage is revealed in a complex chemical reaction or when the mutual effect of two such stages is absent, as was observed in our experiments.

The variant of the kinetic scheme (3)-(7) presented in the form of differential equations was numerically integrated on a computer. The k_3 , k_4 , k_5 , k_6 , and k_7 parameters were estimated for each experimental kinetic dependence. Integration was performed by the Runge-Kutta method with minimization of the sum of the squares of the differences between the experimental and calculated values of the observed variable at ratios of the concentrations of the starting components PO and H₂S $\sigma = 0.82$ and $\sigma = 1.88$, and the minimization was performed by the Marquardt method.¹²

The reaction under study proceeds with a change in the volume, and the kinetic curves were obtained in "amount of substance (mol)—time" coordinates. For convenience of computer simulation of the kinetic scheme and comparison of the calculated and experimental kinetic curves, instead of the reaction rate constants k_4 , k_6 , k_7 ($L^2 mol^{-2} s^{-1}$) and k_3 , k_5 ($L mol^{-1} s^{-1}$), we used in calculations the corresponding values k'_4 , k'_6 , k'_7 ($mol^{-2} s^{-1}$) and k'_3 , k'_5 ($mol^{-1} s^{-1}$) that are independent of change in the volume during the reaction. The k_4 , k_6 , k_7 and k'_4 , k'_6 , k'_7 constants are interrelated by the correlation $k = k' \cdot V^2$, and the k_3 , k_5 and k'_3 , k'_5 constants are related by the correlation k =k'V, where V is the averaged volume of the system, in our experiments V = 0.1 L.



Fig. 5. Influence of k'_3 on the time dependences of the amounts of H₂S (2, 2'), PO (1, 1'), and HPT (3, 3') calculated for reactions (3)-(7) at $\sigma = 1.88$ and unchanged values of certain constants ($k'_4 = 2.1 \cdot 10^{-6}$, $k'_6 = 3.6 \cdot 10^{-4}$, $k'_7 = 1.7 \cdot 10^{-3} \text{ mol}^{-2} \text{ s}^{-1}$ and $k'_5 = 8.3 \cdot 10^{-7} \text{ mol}^{-1} \text{ s}^{-1}$); for 1, 2, and 3, $k'_3 = 5.6 \cdot 10^{-9}$; for 1', 2', and 3', $k'_3 = 1.5 \cdot 10^{-8} \text{ (mol}^{-1} \text{ s}^{-1})$. N is the amount of compounds.

The results of numerical integration were obtained in the form of the amounts of all substances participating in the reaction that correspond to certain moments, at specified values of rate constants. The time dependences of the amounts of substances coincide satisfactorily with the experimental kinetic curves of consumption of the starting substances and accumulation of the reaction products with the following reaction rate constants: k'_4 = 2.1 · 10⁻⁶ (mol⁻² s⁻¹), k_4 = 2.1 · 10⁻⁸ (L² mol⁻² s⁻¹); k'_6 = 3.6 · 10⁻⁴ (mol⁻² s⁻¹), k_6 = 3.6 · 10⁻⁶ (L² mol⁻² s⁻¹) k'_7 = 1.7 · 10⁻³ (mol⁻² s⁻¹), k_7 = 1.7 · 10⁻⁵ (L² mol⁻² s⁻¹); k'_5 = 8.3 · 10⁻⁷ (mol⁻¹ s⁻¹), k_5 = 8.3 · 10⁻⁸ (L mol⁻¹ s⁻¹); for σ = 0.82, k'_3 = 2 · 10⁻⁸ (mol⁻¹ s⁻¹), k_3 = 2 · 10⁻⁹ (L mol⁻¹ s⁻¹); for σ = 1.88, k'_3 = 3 · 10⁻⁹ (mol⁻¹ s⁻¹), k_3 = 3 · 10⁻¹⁰ (L mol⁻¹ s⁻¹).

The error in determination of the reaction rate constants is 15-20%. The differences in the k_3 values for $\sigma = 0.82$ and $\sigma = 1.88$ can be associated with the different treatments of the reactor surface before the experiment.

Comparison of the rate constants of reactions (6) and (4) of H_2S with PO showed a great difference between the catalytic effects of DHPS and HPT: their ratio $k_6/k_4 = 1.8 \cdot 10^2$. Comparison of the rate constants of reactions (7) and (6) shows that in the presence of DHPS epoxide reacts with HPT more rapidly than with H_2S : $k_7/k_6 = 4.7$. A similar result has previously been obtained⁴ for the H_2S -PO system (20 °C, water as solvent) when the ratio of the maximum rates of analogous reactions was equal to 2.6.

It is noteworthy that the rate constants of reactions (3)—(7) are effective, and the reaction under study is, in fact, more complex than that presented by the kinetic scheme. For example, the formation of intermediate



Fig. 6. Influence of k'_3 on the time dependences of the amounts of H₂S, PO (1', 2', 3'), and HPT (1, 2, 3) calculated for reactions (3)–(7) at $\sigma = 1.0$ ($[H_2S]_0 = [PO]_0$) and unchanged values of the constants indicated in Fig. 5 and $k'_3 = 1.4 \cdot 10^{-4}$ for 1 and 1'; $k'_3 = 1.4 \cdot 10^{-5}$ for 2 and 2'; $k'_3 = 1.4 \cdot 10^{-6}$ (mol⁻¹ s⁻¹) for 3 and 3'. N is the amount of compounds.

Additive	Amount /mol L ⁻¹	k'3 /mol ⁻¹ s ⁻¹	k_3 /L mol ⁻¹ s ⁻¹	k_i /L ² mol ⁻² s ⁻¹	γ*
Water	1.40	3.6 • 10 ⁻⁵	3.6 • 10 ⁻⁶	2.6 - 10 ⁻⁶	1.4
HPT	1.80	4.0 · 10 ⁻⁷	4.0 - 10-8	2.3 · 10 ⁻⁸	$1.2 \cdot 10^{-2}$
2-Hydroxy- ethane-1-thiol	1.20	$1.9 \cdot 10^{-7}$	1.9 · 10 ⁻⁸	1.6 · 10 ⁻⁸	0.8 • 10-2
DHPS	0.57	1.1 • 10 ⁻⁵	1.1 - 10-6	1.9 • 10-6	1.0

Table 2. Relative efficiency of homogeneous catalytic additives

* γ is relative efficiency.

reactive complexes is possible for epoxide with hydroxyalkanethiol and epoxide with hydroxylalkanesulfide, as was established by the kinetic and spectral systems.¹³

The study of the effect of the rate constants of particular stages on the process under study showed that both the position and the height of a maximum on the curve of HPT accumulation depend on the k'_3 , k'_4 , k'_6 , and k'_7 constants. The influence of the k'_3 constant, which characterizes the reaction of H₂S with PO independent of autocatalysis, is of special interest.

The effect of the k'_3 constant on changing the amounts of the H₂S and PO reagents and the HPT product over time at unchanged values of other constants is presented in Figs. 5 ($\sigma = 1$) and 6 ($\sigma = 1.88$). As seen in Figs. 5 and 6, when k'_3 increases by 10⁵ times (from 10⁻⁹ to 10⁻⁴ mol⁻¹ s⁻¹), the maximum on the curve of HPT accumulation is shifted toward a decrease in the overall reaction duration, and the amplitude of the maximum changes insignificantly.

We proposed a criterion for estimation of the catalyst efficiency for the reaction under study, assuming that catalysts participate only in stages determining the k'_3 constant, and the reaction mechanism is the same for all catalysts. Probable exceptions are metal alcoholates, potassium hydrosulfide, and tertiary amines. Since these catalysts are the most efficient in these cases, the reaction mechanism becomes ionic. Hence, kinetic scheme (3)-(7) is not appropriate for them. For example, in the case of triethylamine, this assumption is based on the following facts. It was qualitatively established that when triethylamine is saturated with hydrogen sulfide, its electric conductivity increases; for the triethylamine-2hydroxyalkane-I-thiol-epoxide system, the ionic character of the reaction was experimentally established; and the kinetic parameters were quantitatively determined for all its stages. 14-17

For quantitative comparison of the efficiency of catalytic additives at unchanged values of rate constants $k'_4 = 2.1 \cdot 10^{-6}$, $k'_6 = 3.6 \cdot 10^{-4}$, $k'_7 = 1.7 \cdot 10^{-3} \text{ mol}^{-2} \text{ s}^{-1}$, and $k'_5 = 8.3 \cdot 10^{-7} \text{ mol}^{-1} \text{ s}^{-1}$, we chose the k'_3 values to obtain the maximum coincidence of the experimental and calculated kinetic curves.

We determined the k'_3 values for homogeneous catalytic additives. The k'_3 values, the corresponding

Table 3. Relative efficiency of heterogeneous catalytic addi	tives

Additive	Amount /g	k ₃ /L mol ⁻¹ s ⁻¹	Ŷ
10S-3*	1.05	6 · 10 ⁻⁵	1.0
Anion-exchange			
resin AB-17	1.09	$5 \cdot 10^{-7}$	$8 \cdot 10^{-3}$
Fe ₂ O ₃	1.14	≤5 · 10 ⁻⁷	≤8 · 10 ⁻³
AC**	1.00	2 - 10-7	$3 \cdot 10^{-3}$
PbO ₂	1.00	7 - 10-8	$1 \cdot 10^{-3}$
KU-2	1.00	≤2.7 · 10 ⁻⁸	4 · 10 ⁻⁵

* Ion-exchange resin. ** Active carbon.

 k_3 values containing the catalyst concentration as the constant $k_3 = k_i [M]_0$, where M is the catalyst, and their relative efficiencies (γ) are presented in Table 2. The k_1 value for DHPS was taken as unity. The catalytic activities of water and sulfide are almost equal and exceed those of both thiols ~100 times. The rate constant $k_1 = 2.3 \cdot 10^{-8} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$, obtained under conditions where HPT was used as the catalytic additive, and $k_4 = 2.1 \cdot 10^{-8} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$, when thiol acts in the autocatalytic reaction (4), coincide nicely.

The k'_3 values for the heterogeneous catalysts were similarly determined. In all cases, to estimate the efficiency of this group of catalysts, they were taken in the same weight amounts (1 g). The efficiencies of the catalyzing additives are compared to that of IOS-3. As seen in Table 3, the catalytic additive IOS-3 is the most efficient, and cation-exchange resin KU-2 is the least, for which k'_3 virtually does not differ from k'_3 obtained without additives (only with the effect of the reactor wall).

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