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Physical Chemistry

G. V. Rakova, A. K. Avakyan, L. M. Romanov, N. S. Enikolopyan

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

Physical Chemistry

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Kinetics of the Cationic Polymerization of Trioxane

(Presented by Academician N. N. Semenov, February 21, 1964)

The general kinetic picture of the cationic polymerization of trioxane in solution is as follows: at first an induction period is observed, then the process accelerates, reaching a maximum rate, and after this passes into a stage of retardation. The magnitude of these characteristics depends on the concentration of the monomer, the initiator, and the temperature.

We studied the dependence of the maximum rate of polymerization on the initial concentrations of monomer and catalyst (tin tetrachloride) at 30°.

It was established that the maximum rate of trioxane polymerization in methylene chloride and in nitrobenzene depends linearly on the concentration of tin tetrachloride (Fig. 1). This permits the conclusion that either the entire initiator participates in the formation of active centers, or some proportional part of it participates, while the death of active centers occurs by a first-order process with respect to the initiator. For the maximum rate we obtained a fourth order with respect to trioxane in methylene chloride and a second order in nitrobenzene (Fig. 2). Determination of the reaction order carried out in the course of the process (solvent—methylene chloride) also indicates a strong dependence of the polymerization rate on the initial monomer concentration (order higher than 4th).*

Fig. 1. Dependence of W_{max} on the concentration of tin tetrachloride.
a—in methylene chloride at 30° ($C_{\text{M}} = 2.7$ mol/l);
b—in nitrobenzene at 30° (1—$C_{\text{M}} = 3.2$ mol/l; 2—$C_{\text{M}} = 5.3$ mol/l).

It is possible that the high order is connected with the initiation stage. It is known that tin tetrachloride forms stable complexes with a number of organic compounds, in particular with simple ethers (for example, $SnCl_4 \cdot 2(C_2H_5)_2O$). Since trioxane has bonds similar to those in simple ethers, it may be assumed that it is also capable of forming complexes with $SnCl_4$. Then

$$2\mathrm{T} + \mathrm{S} \underset{K}{\rightleftharpoons} \mathrm{Q_T}, \tag{1}$$

where T is trioxane, S is the catalyst, $\mathrm{Q_T}$ is the complex of the catalyst with two trioxane molecules, and K is the equilibrium constant of the formation reaction complex. A third molecule of trioxane participates in the activation of the complex Q_T

$$Q_T + \mathrm{T} \xrightarrow{k_0} X, \tag{2}$$

where X is the active center, k_0 is the initiation constant. Chain growth occurs by addition of new monomer molecules to the active center

$$X_i + \mathrm{T} \xrightarrow{k_p} X_{i+1}, \tag{3}$$

where k_p is the chain-growth constant, X_i and X_{i+1} are active polymer molecules with i and $(i+1)$ units. Deactivation of the active polymerization centers may occur:

$$X_i \xrightarrow{k_r} \text{termination}, \tag{4}$$

where k_r is the termination constant. In the steady state:

$$\frac{dX}{dt} = k_0[Q_T][\mathrm{T}] - k_r[X] = 0, \tag{5}$$

whence

$$[X] = \frac{k_0}{k_r} K[S][\mathrm{T}]^3. \tag{6}$$

Fig. 2. Dependence of $\lg W_{\max}$ on $\lg C_M$.
a—in methylene chloride at 30° ($C_K = 4 \cdot 10^{-3}$ mol/l), b—in nitrobenzene at 30° ($C_K = 1 \cdot 10^{-3}$ mol/l)

Substituting the value for X into the rate equation

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* It should be noted that Kern [1] obtained a high order both with respect to trioxane and with respect to initiator in polymerization in methylene chloride under the action of $\mathrm{BF_3}$.

$$W_{\max} = k_p[C][\mathrm{T}], \tag{7}$$

we obtain

$$W_{\max} = \frac{k_0 k_p K}{k_r}[C][\mathrm{T}]^4, \tag{8}$$

i.e., the polymerization rate depends on the trioxane concentration to the fourth power.

Nitrobenzene, being a strongly polar agent, is probably capable of displacing trioxane from complex compounds with tin tetrachloride, and then

$$S + R \rightleftarrows Q_R,$$

where R is nitrobenzene, Q_R is the complex with nitrobenzene. Otherwise the scheme remains the same.

As a final result we obtain that the maximum polymerization rate depends on the trioxane concentration to the second power.

The polymerization mechanism of trioxane considered here does not claim to be unambiguous. Cokley and Dainton (2) showed that, in the polymerization of styrene in carbon tetrachloride and nitrobenzene under the influence of $SnCl_4$, third order is observed in the first solvent, and first order with respect to monomer in the second. This fact is explained by the circumstance that in CCl_4 the initiating complex ionizes with participation of the monomer, whereas in $C_6H_5NO_2$ it does so only under the influence of the latter.

It is possible that the results we obtained on the reaction order with respect to trioxane in CH_2Cl_2 and $C_6H_5NO_2$ are a consequence of the difference in the polarity of the solvents.

Experimental Part

The kinetics of trioxane polymerization were measured by the dilatometric method; *n*-heptane was used as the sealing layer in the dilatometer. The reaction ampoules were filled with trioxane, solvent, and catalyst under vacuum and in an atmosphere of dry argon. Trioxane in ether solution was treated with metallic sodium, the ether was distilled off, and then the trioxane was distilled over metallic sodium on a rectification column. Additional drying was carried out in a vacuum apparatus.

Methylene chloride was washed with concentrated sulfuric acid, alkali solution, and water, and dried with calcium chloride, silica gel, and aluminosilicate.

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Nitrobenzene was subjected to fractional crystallization, dried with phosphorus pentoxide, distilled, and stored in an argon atmosphere. Tin tetrachloride was boiled over phosphorus pentoxide and distilled. Solutions of $SnCl_4$ were stored under argon.

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1. W. Kern, V. Jaacks, International Symposium on Macromolecular Chemistry, 2, Moscow, 1960, p. 280.
2. R. Colclough, F. Dainton, *Trans. Farad. Soc.*, **53**, 1031 (1957); **54**, 886, 894, 898, 901 (1958).

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

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