Chemistry

Academician V. A. KARGIN, V. A. KABANOV, O. V. KARGINA

1963

SovietRxiv

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Abstract

Full Text

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Academician V. A. KARGIN, V. A. KABANOV, O. V. KARGINA

PREPARATION AND STUDY OF THE CATALYTIC PROPERTIES OF HIGH-MOLECULAR-WEIGHT POLYSTYRENESULFONIC ACID

The hydrolysis of esters by low-molecular-weight acids has been well studied. We carried out a comparative study of the kinetics of ethyl acetate hydrolysis in the presence of a strong high-molecular-weight acid—polystyrenesulfonic acid (PSSA)—and toluenesulfonic acid (TSA), a low-molecular-weight acid modeling a PSSA unit. The study was undertaken in order to determine whether the rate of hydrolysis changes on going from a monomeric catalyst to a polymeric one possessing a chain structure. This question is of general interest for the study of the specific features of the catalytic properties of high-molecular-weight compounds and for elucidating approaches to the modeling of enzymatic processes.

PSSA was obtained by photopolymerization of styrenesulfonic acid in 70% aqueous solution in the presence of 0.01% $K_2S_2O_8$ at 10°. The PSSA used in the work had a specific viscosity of a 1% aqueous solution at 30° equal to 7.2.

Macromolecules of PSSA, owing to the electrostatic repulsion of like-charged dissociated sulfo groups, have extended conformations in aqueous solutions. Accordingly, upon their aggregation, which occurs during concentration of the solutions and removal of solvent, asymmetric fibrillar structures are formed (Fig. 1). Concepts of extended conformations of PSSA chains in aqueous solutions may be of great importance for understanding the mechanism of hydrolysis.

Fig. 2. Dependence of ln k_{ef} on reciprocal temperature for PSSA (1) and TSA (2) during hydrolysis in aqueous solution. Acid concentration $4.0 \cdot 10^{-3}$ N. Ethyl acetate concentration 0.128 mol/l

Table 1 presents data on the dependence of the effective rate constants for ethyl acetate hydrolysis in the presence of PSSA ($k_{ef.p}$) and TSA ($k_{ef.m}$) on acid concentration (the PSSA concentration is given calculated per base mole).

It is seen from the table that, at the same acid concentration, hydrolysis catalyzed by the polymer proceeds faster than hydrolysis in the presence of the monomer over the entire concentration interval studied. At the same time, the ratio $k_{\mathrm{ef.p}}/k_{\mathrm{ef.m}}$ increases as the catalyst concentration decreases. However, the total activation energies of hydrolysis in the presence of PSSA and TSA proved to be the same and equal to ~ 15 kcal/mol (Fig. 2).

The rate of hydrolysis of ethyl acetate (W) in excess water (a first-order reaction) can be expressed by the equation

$$W = k \quad [\dot{\mathrm{A}}\mathrm{H}^+], \tag{1}$$

where k is the true rate constant of hydrolysis, $[\dot{\mathrm{A}}\mathrm{H}^+]$ is the concentration of the protonated form of ethyl acetate—the active intermediate pro-

product, which by a monomolecular mechanism decomposes into ethyl alcohol and acetic acid. The increase in the rate of hydrolysis in the presence of PSSA may occur either as a result of an increase in k_{true}, or owing to an increase in $[\mathrm{AH}^+]$, or, finally, as a result of the joint action of these two factors. We have no grounds to believe that, on replacing a monomeric acid by a polymeric one, the value of the true rate constant for the monomolecular decomposition of the intermediate product changes, especially since the activation energies of the process in both cases prove to be identical. It remains to be assumed that in the presence of PSSA the stationary concentration of the protonated form of ethyl acetate $[\mathrm{AH}^+]$ increases. At low acid concentrations this quantity is expressed by the equation:

$$[\mathrm{AH}^+] = K'_A[\mathrm{A}]\frac{\gamma_{\mathrm{H_3O^+}}\gamma_{\mathrm{A}}}{\gamma_{\mathrm{AH^+}}}[\mathrm{H_3O^+}], \tag{2}$$

where $[\mathrm{A}]$ is the concentration of ethyl acetate, $[\mathrm{H_3O^+}]$ is the concentration of hydroxonium ions, and γ are the corresponding activity coefficients,

$$K'_A = \frac{K_A}{[\mathrm{H_2O}]\gamma_{\mathrm{H_2O}}},$$

where K_A is the basicity constant of ethyl acetate. Then the expression for the effective rate constant of hydrolysis, determined experimentally, is written as:

$$k_{\mathrm{eff}} = k_{\mathrm{true}}K'_A[\mathrm{H_3O^+}][\mathrm{A}]\frac{\gamma_{\mathrm{H_3O^+}}\gamma_{\mathrm{A}}}{\gamma_{\mathrm{AH^+}}}. \tag{3}$$

At identical concentrations of ethyl acetate and acid, k_{eff} may change when the effective value of the product of the activity coefficients changes. The main reason for the increase in the specific rate of hydrolysis on going from TSA to PSSA is apparently the increase in the concentration of hydroxonium ions near the polymer chains.

Table 1

Dependence of the effective rate constants of hydrolysis of ethyl acetate in the presence of PSSA ($k_{\text{eff,p}}$) and TSA ($k_{\text{eff,m}}$) on the acid concentration in aqueous medium. Temperature 60°, ethyl acetate concentration 0.128 mol/l

Acid concentration (N)	$k_{\text{eff,p}} \cdot 10^3$ (min^{-1})	$k_{\text{eff,m}} \cdot 10^3$ (min^{-1})	$\frac{k_{\text{eff,p}}}{k_{\text{eff,m}}}$
0.063	8.8	6.9	1.3
0.034	4.75	3.6	1.3
0.0078	1.3	0.77	1.7
0.0040	0.64	0.35	1.8

Indeed, in equally concentrated solutions of PSSA and TSA the volume distribution of one and the same number of hydroxonium ions differs substantially. If, in the case of a solution of a monomeric acid, the hydroxonium ions are uniformly distributed throughout the volume of the solution, then in the case of a polymer, where the ionized sulfo groups are bound into molecular chains, each macroanion, owing to electrostatic attraction, is surrounded by a "hydroxonium cloud," in which the concentration of H_3O^+ ions is substantially higher than their average concentration in the solution. For strong low-molecular-weight acids it is known that, on going from dilute solutions to concentrated ones, the value of the activity coefficient passes through a minimum. In strong acid solutions the activity coefficient increases with concentration and reaches values substantially greater than 1. Thus, for HCl, on going from a concentration of $5 \cdot 10^{-3}N$ to $10N$, the value of γ, initially equal to 0.947, decreases and reaches a minimum of 0.762 at a concentration of $0.5N$, and then increases to 10.65 (1). An effect analogous to the effect of increasing the activity of H_3O^+ ions probably occurs in the immediate vicinity of the polymer chains, where, as a result, the rate of hydrolysis increases noticeably. The increase is not compensated by a decrease in the rate of hydrolysis in the regions

To the article by V. A. Kargin, V. A. Kabanov, O. V. Kargina, p. 845

Fig. 1. Electron-microscopic image of PSSK. The sample was obtained from a 0.01% aqueous solution. 120000×

To the article by S. V. Kuz' mina, p. 964

Fig. 1. Retrogradely altered neuron from the inferior mesenteric ganglion 7 days after removal of the spinal ganglia D_6–L_4 on both sides. Toluidine blue stain. Oc. 10, obj. 100×, imm.

Fig. 2. Retrogradely altered neuron from the celiac ganglion 14 days after removal of the D_{10}–L_3 spinal ganglia on both sides. Toluidine blue stain. Oc. 10, obj. 100×, imm.

of the solution depleted in H_3O^+ ions. As a result, the effective rate constant of hydrolysis, with a uniform distribution of protons (the case of a monomeric acid), proves to be lower than in the presence of the polymer. Naturally, the more strongly the solution is diluted, the more strongly the average concentration of H_3O^+ in the solution differs from their high local concentration near the polymer chain. As the concentration of the solutions is increased, this difference is gradually smoothed out, which is manifested in a decrease in the ratio $k_{\mathrm{eff,p}}/k_{\mathrm{eff,m}}$ (see Table 1).

Thus, the polymeric acid possesses specific catalytic properties that distinguish it from the corresponding monomeric acid. The distinctive feature of the polymeric catalyst is that, in aqueous media, it is more active than the monomeric one. This feature is entirely associated with the chain structure of PSSA.

Moscow State University
named after M. V. Lomonosov

Received
31 July 1963

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