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Polymer-catalyzed hydrolysis of *p*-nitrophenyl butyrate in an oil/water emulsion

I. M. Okhapkin,[a]★ E. E. Makhaeva,[b] and A. R. Khokhlov[a,b]

[a]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (495) 135 5085. E-mail: okhapkin@polly.phys.msu.ru
[b]*Department of Physics, M. V. Lomonosov Moscow State University,*
1 Leninskie Gory, 119992 Moscow, Russian Federation.
Fax: +7 (495) 939 2988. E-mail: khokhlov@polly.phys.msu.ru

Catalysis of hydrolytic decomposition of *p*-nitrophenyl butyrate with the copolymer of *N*-vinylcaprolactam and *N*-vinylimidazole in an *n*-dodecane—water emulsion was studied. The reaction rate in the emulsion is higher than that in a solution containing no emulsified dodecane particles. The data obtained indicate that the reactions involving the surface-active substrate and catalyst can be accelerated by interfaces.

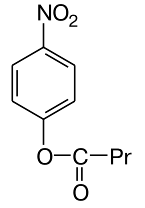
Key words: *N*-vinylimidazole, hydrolysis, emulsion, surface reactions.

One of the main conditions for the synthesis of target products of chemical transformations is the choice of catalyst. An important feature affecting the properties of a catalyst—substrate pair is the physicochemical interaction of a substrate with a carrier of catalytically active groups. This specific feature gave rise to the creation of synthetic hydrophobic polymers capable of adsorbing a substrate. These polymers enable increasing in the reaction rates compared to low-molecular-weight analogs. Hydrolysis of nitrophenol derivatives was studied as an example; the reaction rate increased with an increase in hydrophobicity of the polymeric chain,[1—5] and in some cases the reaction kinetics obeyed the Michaelis—Menten equation.[6,7]

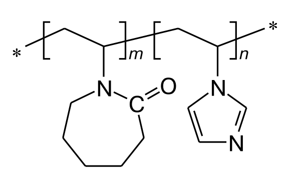
The physicochemical interaction of a substrate with carrier of catalytically active groups plays an important role in micellar catalysis. Reactions in micellar systems are accelerated due to the absorption of the substrate and catalyst by micelles, which is accompanied by the considerable enhancement of their local concentration inside the micelles. In most cases, this absorption is caused by both hydrophobic and electrostatic interactions: micelles formed of ionogenic surfactants are mainly efficient.[8] Similar cases of reaction acceleration were also described[9] for microemulsions stabilized by ionogenic surfactants.

Adsorption of surfactants at the interface is an alternative method for concentrating in a small room. Adsorption of such substances is characterized by high energy gain and occurs in the nanosized surface layer due to which the local concentration on the surface sometimes exceeds the concentration in the solution by several orders of magnitude. As shown theoretically,[10,11] concentrating of the surface-active substrate and catalyst in an ultrathin layer of the interface of a dispersed system (emulsion) can increase the rate of catalyzed reaction.

The purpose of the present study is to check this opportunity. Hydrolysis of *p*-nitrophenyl butyrate (NPB) with catalytic participation of the copolymer of *N*-vinylcaprolactam and *N*-vinylimidazole (PVC-VI) was chosen as the reaction under study.



NPB



PVC-VI

The substrate was chosen from the library of substrates of similar structure: esters of *p*-nitrophenol with acetic, propionic, butyric, caproic, caprylic, and laurylic acids and phenylalanine. *p*-Nitrophenyl butyrate demonstrated the optimal properties from the viewpoint of the surface activity, solubility in water, and the rate of spontaneous hydrolysis (in the absence of PVC-VI). *n*-Dodecane was chosen as the disperse phase of the emulsion, and water was the disperse medium.

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Experimental

p-Nitrophenyl butyrate (Fluka), *n*-dodecane (Acros), and the copolymer of *N*-vinylpyrrolidone and acrylic acid (PVP-AA) (Aldrich, M_w = 96000, VP : AA = 75 : 25) were used without additional purification. The PVC-VI copolymer (M_w = 15000, VC : VI = 80 : 20) was synthesized according to a previously described procedure.[12] The molecular weight of the synthesized copolymer was determined using static light scattering on an ALV-CGS-8F laser goniometer, and the copolymer composition was determined by potentiometric titration using a known procedure.[12] Water purified in a Milli-Q unit was used for the preparation of solutions. Emulsions were prepared by sonication of *n*-dodecane in aqueous solutions in a Bandelin HD-2200 unit. The content of the dispersion phase was 1 vol.%. To stabilize emulsions, the PVP-AA copolymer was added to all dispersed solutions to a concentration of 0.02 g L^{-1}.

The rate of hydrolysis was monitored spectrophotometrically by an increase in the absorbance of the liberated *p*-nitrophenoxide anion (λ = 402 nm). All experiments were carried out in a phosphate buffer (concentration of phosphate ions 0.5 mmol L^{-1}, pH 7.4). The concentration of the catalytically active copolymer PVC-VI was 0.05 g L^{-1}. For monitoring of the reaction rate in a turbid medium, the emulsion was filtered before measurements through a Millex SLGV R33 filter (Millipore) with a pore diameter of 0.22 μm. Aliquots were taken from the reaction medium at 25 °C at specific times and rapidly filtered into a quartz cell, and the absorbance of the resulting transparent solution was recorded at λ = 402 nm. Blank (homogeneous) solutions were studied according to a similar procedure, and they were preliminarily sonicated under the conditions of emulsion preparation. The reaction rate was calculated by the formula

$$V = dA/dt \cdot \varepsilon^{-1} \cdot F^{-1},$$

where dA/dt is the rate of absorbance change for the *p*-nitrophenoxide anion at 402 nm, ε is the extinction coefficient of the *p*-nitrophenoxide anion (18500 L mol^{-1} cm^{-1}), and F is the fraction of the *p*-nitrophenoxide anion of the total content of *p*-nitrophenol (pK_a = 7.15)[13] in the solution at pH 7.4 (F = 0.6).

Results and Discussion

The chemical structures of PVC-VI and NPB assume that they possess surface activity at the oil—water interface and, therefore, can be concentrated on the surface of emulsion droplets, which will accelerate hydrolysis if the reaction occurs in the surface layer (nanoreactor).

It is known that *p*-nitrophenol esters undergo spontaneous hydrolysis in neutral (pH 6—8) aqueous solutions; the reaction is catalyzed by both hydroxide ions and any other basic ions, for instance, phosphate ions. Therefore, in the present work the catalytic reaction was studied along with spontaneous hydrolysis involving hydroxide and phosphate ions. The plots of the reaction rate of NPB hydrolysis *vs.* its concentration under different conditions are shown in Fig. 1, and the calculated pseudo-first-order rate constants with respect to the substrate are given in Table 1.

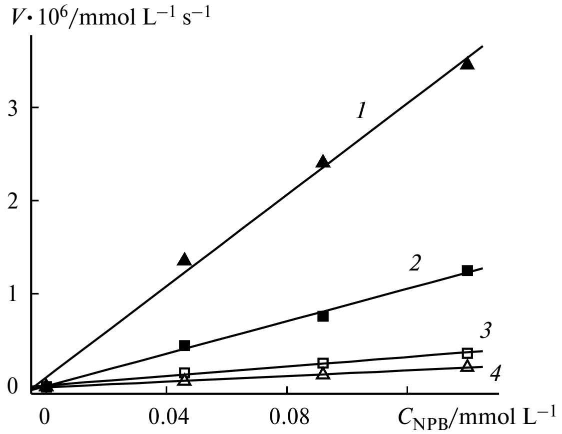

Fig. 1. Kinetic plots of NPB hydrolysis in the presence of PVC-VI in the emulsion (*1*) and in the homogeneous solution (*2*) and spontaneous hydrolysis (in the absence of PVC-VI) in the homogeneous solution (*3*) and in the emulsion (*4*).

Table 1. Rate constants of NPB hydrolysis under different conditions

Process	Rate constant $\cdot 10^5/s^{-1}$	
	in emulsion	in homogeneous solution
Hydrolysis in the presence of PVC-VI	2.4 (k_1)	0.87 (k_2)
Spontaneous hydrolysis (in the absence of PVC-VI)	0.15 (k_3)	0.26 (k_4)
Contribution of PVC-VI to hydrolysis	2.25 ($k_5 = k_1 - k_3$)	0.62 ($k_6 = k_2 - k_4$)

The data presented (see Fig. 1 and Table 1) show that in the presence of PVC-VI the reaction rate in the emulsion is by several times higher than that in the homogeneous solution. Experiments on spontaneous hydrolysis show no acceleration of the reaction in the emulsion compared to that in the homogeneous solution; on the contrary, it is somewhat retarded. Therefore, the reaction acceleration in the emulsion can be caused only by the presence of the polymeric catalyst. The data in Table 1 also show that the contribution of spontaneous hydrolysis to the overall rate is rather high and should be taken into account when determining the contribution of PVC-VI. Subtracting the contribution of spontaneous hydrolysis from the overall reaction rate, one can determine the reaction rate under the catalytic effect of PVC-VI in both the emulsion and homogeneous solution (see Table 1). As a result, the reaction rate for catalysis by PVC-VI is much higher in the emulsion than that in the homogeneous solution. Thus, the acceleration of the NPB hydrolysis reaction in the emulsion is observed in the presence of the surface-active catalyst PVC-VI and is absent in the case of spontaneous hydrolysis when surface-inactive hydroxide and phosphate ions are catalytic agents. This fact supports undoubtedly the hypothesis that NPB hydrolysis in the presence of PVC-VI is accelerated due to the reaction in the surface layer of emulsion droplets, where both the substrate and catalyst are concentrated through adsorption. It is noteworthy that NPB can also be concentrated in the surface layer of emulsions during spontaneous hydrolysis. However, no acceleration is observed in this case, because ions are usually prone to desorption from hydrophobic interfaces and the surface layer is depleted in the catalyst. The observed decrease in the spontaneous hydrolysis rate in the emulsion (see Table 1, Fig. 1) is probably caused by both this factor and the fact that a portion of the substrate can be transferred from the aqueous phase to the dodecane phase in which no reaction occurs.

Thus, the hydrolysis of *p*-nitrophenyl butyrate catalyzed by the *N*-vinylcaprolactam—*N*-vinylimidazole copolymer in a 1% emulsion of dodecane in water occurs much more rapidly than that in the homogeneous solution. This effect was not observed for catalysis by surface-inactive hydroxide and phosphate ions. Therefore, it can be asserted that this effect is caused by the occurrence of the reaction in the surface layer of emulsion droplets, where the concentrations of both the substrate (*p*-nitrophenyl butyrate) and catalyst (copolymer of *N*-vinylcaprolactam and *N*-vinylimidazole) possessing surface activity are higher than those in the solution bulk.

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