Cooperative Effects in the Esterolytic Action of Poly-5(6)-vinylbenzimidazole[1a,b]

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The pH–rate profile of the catalyzed solvolysis of sodium 4-acetoxy-3-nitrobenzenesulfonate with poly-5(6)-vinylbenzimidazole reveals enhanced activity over benzimidazole at low, intermediate, and high pH values. At low pH, electrostatic attraction of the negatively charged substrate to the protonated benzimidazole functions enhances the catalytic activity of the neutral benzimidazole fraction. At high pH, terfunctional contributions, involving neutral and anionic benzimidazole fractions on the polymer, make possible the reaction with this substrate whereas a corresponding process is not significant in the catalysis by monomeric benzimidazole. Spectrophotometric titrations afforded the pK_2 of monomer and polymer and enabled correct assessment of the contribution of the benzimidazole anions on the polymer. As a consequence, an important contribution due to terfunctional interactions involving two neutral benzimidazole functions is revealed at intermediate pH. These three kinds of cooperative effects are combined in an inclusive rate equation.

Introduction

Poly-5(6)-vinylbenzimidazole revealed unusual catalytic activity with charged and uncharged substrates.[2] At high pH values the polymer was a better catalyst than benzimidazole with p-nitrophenyl acetate (PNPA) and the negatively charged substrate, 4-acetoxy-3-nitrobenzoic acid (NABA). Benzimidazole anions were found unreactive with the negatively charged substrate. The difference between the monomer and polymer catalysis was explained by the readiness of the benzimidazole functions on the polymer chain for terfunctional interactions, i.e., those involving two benzimidazole groups, one in the neutral and one in the anionic form, in addition to the uncatalyzed nucleophilic reaction. In the anionic region this was expressed mathematically as the combined contribution[2] (eq. 1) where α_1 and α_2 are the fractions of benzimid-

$$k_{cat}(\text{anionic}) = k'_{an}\alpha_2 + k''_{an}\alpha_1\alpha_2 \qquad (1)$$

azole residues in the neutral and anionic forms, respectively.

Though plots of log k_{cat} vs. pH clearly reveal the dependency of the high polymer activity on the anionic fraction of the polymer, it was worthwhile to look for a method that will establish the precise contribution of

the anionic fraction, i.e., to determine in an independent manner the pK_2 of the polymer. Potentiometric titrations were found inappropriate because of the low solubility of the polymer at high pH values. Therefore, spectrophotometric titrations were undertaken in this investigation.

At low pH values, the protonated sites (α_0) of the homopolymer should have attracted the negatively charged substrate by electrostatic forces and should have optimized the catalytic action of the neutral fraction.[2–4] For the absence of this effect with NABA two explanations were forwarded. (1) The benzimidazole groups are too bulky and incapable of cooperative effects (which was in contrast to the reactivity displayed by this polymer at high pH values). (2) The relatively low dissociation constant of NABA in comparison with the homopolymer ($pK_1 = 3.5$) did not supply a sufficient fraction of the substrate in a charged form at low pH.

To test these possibilities the pH–rate profile of poly-5(6)-vinylbenzimidazole with sodium 4-acetoxy-3-nitrobenzenesulfonate (NABS) was investigated over a wide pH range.

Experimental Section

Poly-5(6)-vinylbenzimidazole was prepared as previously described.[2]

Sodium 4-Acetoxy-3-nitrobenzenesulfonate. Sodium 4-hydroxy-3-nitrobenzenesulfonate was prepared according to the method of Kolbe and Gauhe[5] and was converted to the acetylated derivative according to the procedure of Letsinger and Savereide.[3] Recrystallization was affected from benzene–acetic acid mixture.

Anal. Calcd. for $C_8H_6NNaO_7S$: C, 33.9; H, 2.1; N, 4.9; S, 11.3. Found: C, 34.4; H, 2.4; N, 5.1; S, 11.7.

Spectrophotometric Titrations. For the determination of pK_2 three 3×10^{-5} M solutions of poly-5(6)-vinylbenzimidazole were prepared in 0.0288, 0.0481, and 0.0673 M solutions of sodium hydroxide in 30% propanol–water, with the ionic strength adjusted to 0.0967 by KCl. Similarly, 3×10^{-5} M solutions of benzimidazole were prepared in 0.0288, 0.0481, and 0.0962 M sodium hydroxide in the same solvent and the same ionic strength. If A_N is the ultraviolet absorbance of the 3×10^{-5} M solutions at neutrality, A_- is the absorbance of the same concentration of the negative species, A_1 is the total absorbance at base concentration $C_{OH}(1)$, A_2 is the total absorbance at base concentration $C_{OH}(2)$ and K_h is the hydrolysis constant

(1) (a) This paper comprises a portion of the dissertation submitted by T. St. Pierre in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn. (b) For a preliminary report see C. G. Overberger, T. St. Pierre, N. Vorchheimer, C. Yaroslavsky, J. Lee, J. C. Salamone, R. Sitaramaiah, and S. Yaroslavsky, *Trans. N. Y. Acad. Sci.*, 27, 790 1965.

(2) C. G. Overberger, T. St. Pierre, N. Vorchheimer, and S. Yaroslavsky, *J. Am. Chem. Soc.*, 85, 3513 (1963); C. G. Overberger, T. St. Pierre, N. Vorchheimer, J. Lee, and S. Yaroslavsky, *ibid.*, 87, 296 (1965).

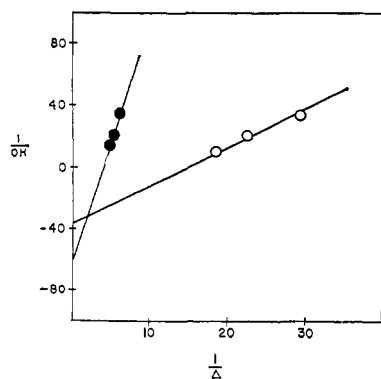(3) R. L. Letsinger and T. J. Savereide, *ibid.*, 84, 114, 3122 (1962); R. L. Letsinger and I. Klaus, *ibid.*, 86, 3884 (1964).

(4) H. Ladenheim, E. M. Loebl, and H. Morawetz, *ibid.*, 81, 20 (1959).

(5) H. Kolbe and F. Gauhe, *Ann.*, 147, 71 (1868).

Figure 1. Plots of 1/OH vs. 1/Δ for poly-5(6)-vinylbenzimidazole (●) and benzimidazole (O).
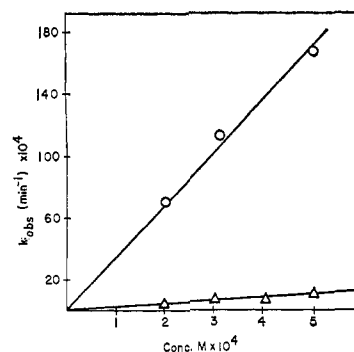

Figure 2. The observed rates of disappearance of NABS as a function of the concentration of poly-5(6)-vinylbenzimidazole (O, pH 8.9) and benzimidazole ($\triangle$, pH 8.4).

for benzimidazole anion, the following relationships hold for any pair of measurements (eq. 2 and 3).[6]

$$K_\mathrm{h} = C_\mathrm{OH}(1) \frac{A_- - A_1}{A_1 - A_\mathrm{N}} = C_\mathrm{OH}(2) \frac{A_- - A_2}{A_2 - A_\mathrm{N}} \quad (2)$$

or

$$A_- = \frac{C_\mathrm{OH}(1)(A_2 - A_\mathrm{N})A_1 - C_\mathrm{OH}(2)(A_\mathrm{N} - A_1)A_2}{C_\mathrm{OH}(1)(A_2 - A_\mathrm{N}) - C_\mathrm{OH}(2)(A_\mathrm{N} - A_1)} \quad (3)$$

Knowing A_- it is possible to calculate K_h and K_2 according to the relationship in eq. 4. The measure-

$$pK_\mathrm{h} = pK_\mathrm{w} - pK_2 \quad (4)$$

ments performed for benzimidazole, including the calculated A_-, are given in Table I.

Table I.[a] Absorbancies of Alkaline Benzimidazole Solutions

$C_\mathrm{OH}(1)$, M	$C_\mathrm{OH}(2)$, M	A_1	A_2	A_-
0.0288	0.0962	0.228	0.248	0.266
0.0481	0.0962	0.238	0.248	0.264
0.0288	0.0481	0.228	0.238	0.270
				Av. 0.267

[a] $\lambda_\mathrm{max} = 278$ mμ, $A_\mathrm{N} = 0.194$, $\mu = 0.0967$.

The measurements performed for poly-5(6)-vinyl-benzimidazole are reported in Table II.

Table II.[a] Absorbancies of Alkaline Poly-5(6)-vinylbenzimidazole Solutions

$C_\mathrm{OH}(1)$, M	$C_\mathrm{OH}(2)$, M	A_1	A_2	A_-
0.0288	0.0673	0.303	0.334	0.368
0.0481	0.0673	0.317	0.334	0.389
0.0288	0.0481	0.303	0.317	0.347
				Av. 0.368

[a] λ_max 272 mμ, $A_\mathrm{N} = 0.140$, $\mu = 0.0967$.

An alternative method of treating these data is to plot 1/OH vs. 1/Δ for eq. 5[7] where Δ is the difference in

$$\frac{1}{\mathrm{OH}} = \frac{1}{\Delta} \times \frac{A_- - A_\mathrm{N}}{K_\mathrm{h}} - \frac{1}{K_\mathrm{h}} \quad (5)$$

(6) H. Walba and R. W. Isensee, J. Am. Chem. Soc., 77, 5488 (1955).
(7) E. A. Westhead, Jr., and H. Morawetz, ibid., 80, 237 (1958).

the absorbancies, $A - A_\mathrm{N}$. The intercept of the curve supplies $1/K_\mathrm{h}$, and A_- can be determined from the slope. The slopes are described in Figure 1. From the direct calculations or from the plots, the pK_2 in 30% propanol–water was determined as 12.4 for the monomer and as ca. 12.2 for the polymer.

By spectrophotometric and potentiometric titrations the pK_1 of the monomer and polymer were previously found as 5.4 and 3.5, respectively.[2] For the pK_1 the polymer behaved like a monoelectrolyte (i.e., $pK_1 = pH + 1.01 \log (1 - \alpha_1)/\alpha_1$. A similar behavior was assumed for pK_2 in the region explored.

Kinetic measurements were done as previously disclosed.[2] Tris(hydroxymethyl)aminomethane buffers, 0.01 M, and ionic strength 0.01, were employed at 26° in 30% propanol–water solutions. Appearance of 4-hydroxy-3-nitrobenzenesulfonate was studied at 360 mμ below pH 7.2, and 400 mμ above pH 7.2.

Results and Discussion

The observed rates of disappearance of sodium 4-acetoxy-3-nitrobenzenesulfonate (NABS) as a function of the concentration of benzimidazole and poly-5(6)-vinylbenzimidazole are described in Figure 2. For the monomer and polymer, rates were first order in substrate and catalyst.

The pH–rate profiles for the monomer and polymer with NABS are presented in Table III. It is seen that the polymer is a catalyst superior to the monomer over the wide pH region studied. While below pH 7 the

Table III.[a] Catalytic Rate Constants for Poly-5(6)-vinylbenzimidazole and Benzimidazole with NABS

	k_cat, l./mole min.	
pH	Poly-5(6)-vinyl-benzimidazole	Benzimidazole
2.45	2.07	. . .
3.50	7.91	. . .
4.20	9.67	. . .
5.20	12.72	2.87
6.00	16.20	. . .
7.20	. . .	3.03
8.40	22.41	2.26
8.90	32.90	. . .
10.10	55.79	. . .

[a] In 30% propanol–water solutions, buffered with 0.01 M tris-(hydroxymethyl)aminomethane and ionic strength 0.01, at 26°.
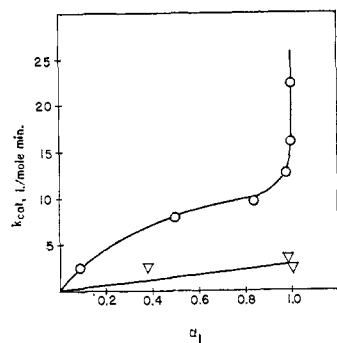
Figure 3. Catalytic rate constants of the solvolysis of NABS catalyzed by poly-5(6)-vinylbenzimidazole (O) and benzimidazole (∇) as a function of neutral benzimidazole fraction.
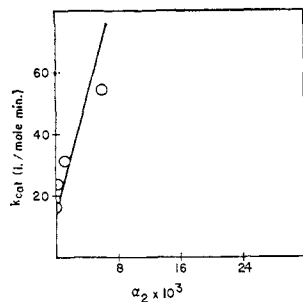

Figure 4. Catalytic rate constants of the solvolysis of NABS catalyzed by poly-5(6)-vinylbenzimidazole as a function of anionic benzimidazole fraction.

Figure 5. pH–rate profiles for the solvolysis of NABS catalyzed by poly-5(6)-vinylbenzimidazole (△) and benzimidazole (O). Solid lines represent calculated curves.

polymer is a more efficient catalyst by a factor of up to 5, above pH 7 the factor may be 18 or even higher. In Figure 3 the catalytic rate constants are plotted against α_1 for the monomer and polymer. The enhanced polymeric rate at $\alpha_1 = 0.75$ or less[8] must be attributed to the electrostatic attraction of the negatively charged substrate to the partially protonated polymer, which improves the catalytic action of the free benzimidazole units. Employing Letsinger's approximations,[3] the catalytic rate constant due to electrostatic attraction of the substrate to the polymer (k_{el}) can be estimated as ca. 7 l./mole min. as compared to k_{neut} for the monomer, which is ca. 3 l./mole min.

The determination of the pK_2 values enables one to gain further insight into the region where part of the polymer is in the anionic form. In Figure 4 the catalytic rate constants for the reaction of the polymer with NABS are plotted against α_2. In contrast to the polymer, the monomer anions do not interact with NABS. A similar situation existed for NABA. The polymeric rate at high pH values was therefore ascribed to a bifunctional catalysis, one possibility of which is that the nucleophilic attack by a neutral benzimidazole function is being catalyzed by benzimidazole anion as a general base (cf. the second term in eq. 1). From Figure 4 it is possible to assess the magnitude of k''_{an} for the reaction with NABS, and it is ca. 10⁴ l./mole min.

(8) H. Morawetz in "Chemical Reactions of Polymers," E. M. Fettes, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p. 20.
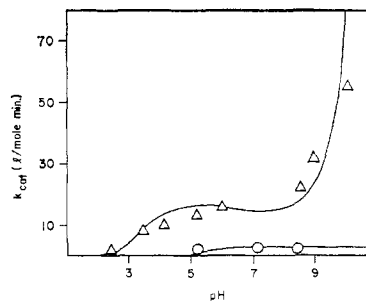
Inspection of Figure 3 reveals that the polymer is highly reactive in the region where α_1 varies from 0.75 to 1.00, i.e., between pH 4.0 and 7.0. In this region the contribution of the anionic fraction is negligible. Also the contribution of the protonated sites should decrease to a minimum. The high rate observed compared to the monomer catalysis in this region (5–6 times higher) is most likely a result of the nucleophilic reaction of neutral benzimidazole with NABS catalyzed by another neutral benzimidazole function as a general base.[9,10] From the intercept of Figure 4 the strictly neutral benzimidazole contribution to the catalytic rate constant can be estimated as close to 16 l./mole min. The uncatalyzed neutral poly-5(6)-vinylbenzimidazole rate constant can be estimated from the rate of monomer catalysis as ca. 2 l./mole min.: therefore the contribution of the catalyzed neutral poly-5(6)-vinylbenzimidazole reaction is ca. 14 l./mole min.

In conclusion, we can summarize the three kinds of cooperative effects in the solvolysis of NABS catalyzed by poly-5(6)-vinylbenzimidazole, i.e., those involving (1) protonated and unprotonated benzimidazoles, (2) two neutral benzimidazoles, (3) one neutral and one anionic benzimidazole functions, in the following mathematical expression.[2,3,11]

$$k_{cat} = k_{el}\alpha_0\alpha_1 f(\alpha_1)\alpha_s + k'_{neut}\alpha_1 + k''_{neut}\alpha_1{}^2 + k''_{an}\alpha_1\alpha_2 \quad (6)$$

At low pH values the first three terms are operating, while the last three terms are involved at high pH values. In Figure 5 the calculated pH–rate profile for the reaction of poly-5(6)-vinylbenzimidazole with NABS based on eq. 6 (solid line) is compared to the experimental points. In the calculation the following rate constants were employed: $k_{el} = 7$, $k'_{neut} = 2$, $k''_{neut} = 14$, and $k''_{an} = 10^4$ l./mole min. Also the calculated pH–rate profile for the monomer is presented.

(9) T. C. Bruice and S. J. Benkovic, J. Am. Chem. Soc., 86, 418 (1964).
(10) J. F. Kirsch and W. P. Jencks, ibid., 86, 833 (1964).
(11) T. C. Bruice and G. E. Schmir, ibid., 80, 148 (1958).