

Decarboxylation of the 6-Nitrobenzoxazole-3-Carboxylate Anion Catalyzed by Cross-Linked Poly(4-Vinylpyridinium) Salts
Catalysis by Cross-Linked Cationic Polymers II.

Noboru Yamazaki¹, Seiichi Nakahama¹, Akira Hirao¹, Juheiji Kawabata¹, Hiromichi Noguchi² and Yasuzo Uchida²

¹ Department of Polymer Science, Tokyo Institute of Technology, Tokyo, 152, Japan

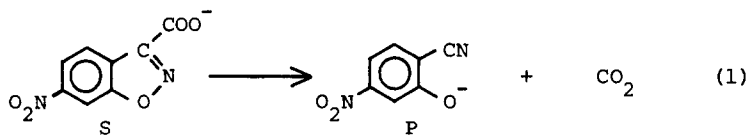
² Department of Industrial Chemistry, Faculty of Engineering, University of Tokyo, Tokyo, 113, Japan

Summary

Catalysis of cationic polyelectrolytes for the decarboxylation of 6-nitrobenzoxazole-3-carboxylate anion was studied in a buffer solution (pH = 9.0). Cross-linked poly(4-vinylpyridinium) salts prepared from 4-vinylpyridine and α, ω -dibromides were used as cationic catalysts. The cross-linked catalysts were found to accelerate markedly the decarboxylation in comparison with the linear water-soluble analogues. Effect of the polymer structure such as the length of $(\text{CH}_2)_x$ linkages between positive charges on the catalytic activity was examined. It was suggested that the acceleration by the cross-linked polymer catalysts would be due to the hydrophobic microenvironment around the catalytic sites.

Introduction

It has been found that the decarboxylation of 6-nitrobenzoxazole-3-carboxylate anion, S, (eq. 1) was accelerated by cationic micelles such as cetyltrimethylammonium bromide (BUNTON et al. 1970), charged polysoaps derived from poly(4-vinylpyridines) (KUNITAKE et al. 1977), and modified polyethylenimines containing apolar lauryl groups (KLOTZ et al. 1976).



The importance of a hydrophobic environment around the catalytic sites in the activation of a substrate anion has been proposed in these studies. The desolvation of the carboxylate anion, S, in the hydrophobic environment is favorable for the stabilization of the charge-delocalized transition state of S, and thereby accelerates the decarboxylation reaction.

We have recently found that cross-linked polystyrene resins having quaternized ammonium chloride groups, I, bring about a marked rate enhancement of the decarboxylation of S as compared with a soluble polymer analogue and a cationic micelle (YAMAZAKI et al. 1979). In the presence of the cross-linked polymers, I, appreciable hypsochromic shifts were observed in the fluorescence maximum wavelength of 6-p-toluidinonaphthalenesulfonate used as a hydrophobic probe, and this observation was taken to suggest that the hydrophobicity around the cationic sites of I is further strengthened. Based on

catalyst calculated from the nitrogen content of elemental analysis.

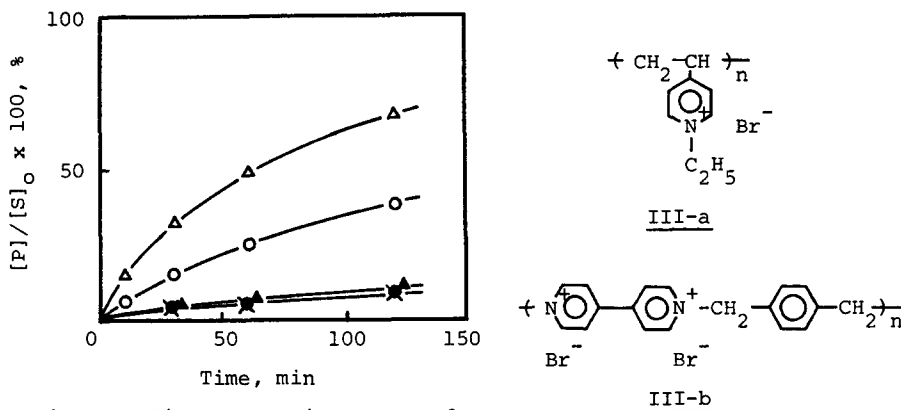


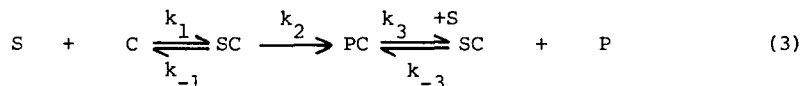
Fig. 1 : Time-conversion Curves for Decarboxylation of S Catalyzed by Soluble and Cross-linked Poly-(4-vinylpyridinium) Salts

$[S]_0, 6 \times 10^{-3} M$; $[C]_0, 1.2 \times 10^{-3}$ eq/l; $30^\circ C$; pH, 9.0

○ : II-a; ▲ : II-f; ● : III-a
▲ : III-b; × : none

Figure 1 shows the time-conversion curves for the decarboxylatic reaction in the presence of an excess of the substrate, i.e., $[S]/[C] = 5$. Evidently the cross-linked polymer catalysts, II-a and II-f, significantly accelerated the decarboxylation of S in the heterogeneic system, while both water-soluble polymer analogues, III-a and III-b, did not exhibit appreciable catalytic effect. It was also noted that the structure of II might influence the rate of decarboxylation.

In a previous paper (YAMAZAKI et al., 1979) we have proposed the following reaction scheme for the decarboxylation of S catalyzed by cross-linked polystyrene resins having quaternary ammonium groups,



The reaction scheme (eq. 3) shows that the substrate anion incorporates onto the active site by ion-exchange, SC, is catalyzed there to afford the product adsorbed at the active site, PC. Then, the product is released into the aqueous phase as a result of ion-exchange between P and S at the catalytic site. We have confirmed experimentally that the substrate anion was rapidly adsorbed quantitatively onto the polymeric catalyst prior to the decarboxylation. This scheme eventually permitted us to derive equation 4 based on two assumptions i.e., $[C]_0 = [SC] + [PC]$ and the steady-state assumption, $d[PC]/dt = 0$ (YAMAZAKI et al., 1979) :

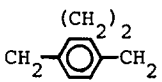
$$\frac{V}{[C]_0} = k_2 - \frac{k_{-3}}{k_3} \cdot \frac{V}{[C]_0} \cdot \frac{[P]}{[S]_0 - [C]_0 - [P]} \quad (4)$$

where V , $[C]_0$ and $[S]_0$ are the apparent rate of release of the product ($d[P]/dt$), initial concentration of the catalyst and that of the substrate, respectively. The value of the first-order rate constant, k_2 , could be evaluated from the intercept of the straight line obtained by plotting $V/[C]_0$ vs. $V[P]/[C]_0$ ($[S]_0 - [C]_0 - [P]$).

The decarboxylation reaction catalyzed by the cross-linked polymers, II, proceeded in a manner quite similar to that by the catalyst I. Thus the same treatment as above was applied to the present system to obtain a good linear relationship for equation 4. The catalytic efficiency of II was then estimated by evaluating the first-order rate constant, k_2 .

TABLE I

First-order Rate Constants for the Decarboxylation of S Catalyzed by Cross-linked and Water-soluble Poly-N-alkylpyridinium Salts ^{a)}

No.	Catalyst	-R-	Rate Constant x 10 ⁴ , sec ⁻¹
1	none		0.06
2	III-a	b)	0.21
3	III-b	b)	0.33
4	II-a	(CH ₂) ₂	5.4 ± 0.3
5	II-f		12.4 ± 0.6


a) 30°C; pH = 9.0 b) The intrinsic viscosities of III-a and III-b measured in 0.4 M KBr at 25°C were 0.03 and 0.06 dl/g, respectively. c) $[S]_0 = 2 \times 10^{-3}M$; $[C]_0 = 4 \times 10^{-2}$ eq/l d) $[S]_0 = 6 \times 10^{-3}M$; $[C]_0 = 1.2 \times 10^{-3}$ eq/l

Table I summarizes the values of k_2 as well as those of the first-order rate constants, k_d , in the homogeneous system (KUNITAKE et al., 1977) for the runs in Figure 1. The value of k_2 for II-f was 210-fold greater than that of k_d for the control reaction carried out in the absence of catalyst (Nos. 1 and 5). Evidently the cross-linked polycationic catalysts (Nos. 4 and 5) are much more effective than the soluble analogues (Nos. 2 and 3). This suggests that the cross-linked polymer chains in II would play an important role for the rate enhancement of the reaction, and that the acceleration by II would also be attributable to the formation of such hydrophobic micro-environment around the catalytic sites as described in the introduction for the catalysts I.

A considerable difference in the catalytic efficiency between the cross-linked catalysts, II-a and II-f suggests the influence of the R linkage between pyridinium cations on the catalytic activity (Nos. 4 and 5 in Table I). In order to investigate the correlation between the hydrophobicity provided by the R group in II and the catalytic activity, variety of II which contain a series of polymethylene, xylylene and oxyethylene groups as R were prepared by the reactions of 4-vinylpyridine with various α, ω -dibromides in bulk and in dimethylformamide.

TABLE II

First-order Rate Constants, k_2 , for the Decarboxylation of S Catalyzed by II ^{a)}

No.	Polymer catalyst	-R-	$k_2 \times 10^4 \text{ sec}^{-1}$	
			II-1 ^{b)}	II-2 ^{b)}
1	II-a	$(\text{CH}_2)_2$	5.4 ± 0.3	-
2	II-b	$(\text{CH}_2)_4$	8.5 ± 0.5	10.9 ± 0.4
3	II-c	$(\text{CH}_2)_6$	12.5 ± 0.4	14.0 ± 0.9
4	II-d	$(\text{CH}_2)_8$	16.6 ± 0.4	-
5	II-e	$\text{CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_2$	-	9.4 ± 0.2
6	II-f	CH_2 -  - CH_2	-	12.4 ± 0.6

a) $[\text{S}]_0 = 6 \times 10^{-3} \text{ M}$; $[\text{C}]_0 = 1.2 \times 10^{-3} \text{ eq/l}$ b) II-1 and II-2 were prepared in bulk and DMF, respectively.

Table II shows the values of first-order rate constants, k_2 , for the decarboxylation of S catalyzed by II. The catalytic efficiency of II increased with the increase in the length of $(\text{CH}_2)_n$ linkage in II (Nos. 1,2,3, and 4). The catalyst having hydrophilic oxyethylene units, II-e, exhibited a lower catalytic efficiency than the catalyst II-d containing the same number of members between pyridinium cations (Nos. 4 and 5). These results suggest that the hydrophobic environment by apolar R group would also cause the rate enhancement of the reaction.

The reaction of 4-vinylpyridine with an α, ω -dibromide in bulk proceeds rapidly at 25°C to give an extremely hard mass (II-1 series), while the same reaction in solution proceeds more slowly to afford a rather soft gel (II-2 series). Therefore, it was suspected that the different reaction conditions might result in a considerable difference in the catalyst structures enough to greatly affect their catalytic activity. However, the catalysts prepared in dimethylformamide did not differ significantly in the catalytic efficiency from the catalysts in bulk (Nos. 2 and 3 in Table II).

A more detailed study on the correlation between the structure of the cross-linked polymers and their catalytic activity is now in progress.

Experimental

Materials. 6-Nitrobenzisoxazole-3-carboxylic acid was prepared by the hydrolysis of methyl 6-nitrobenzisoxazole-3-carboxylate (BORSCHE, 1909; LINDEMANN and CISSEE, 1929) and recrystallized from methanol, mp 167-169°C [lit.: 167-169°C]. Cross-linked poly(4-vinylpyridinium) salts, II, were prepared by the following procedure. Freshly distilled 4-vinylpyridine (20 mmol) was mixed with an α, ω -dibromide (10 mmol) in bulk or in dimethylformamide (10 - 20 ml). The mixture was kept at 25°C for periods of 7 - 14 days. The cross-linked polymer thus formed was triturated in methanol, filtered and washed thoroughly with methanol. After drying in vacuo at 60°C to a constant weight,

it was obtained in the form of a light brown powder in yields of 80 - 100% of the theoretical amounts. The water-soluble poly(4-vinylpyridinium) salt, III-a, and the ionene polymer, III-b, were prepared according to the procedures described in literatures (KABANOV et al., 1967; REMBAUM and NOGUCHI, 1972). The anion exchange capacities of the cross-linked poly(4-vinylpyridinium) salts were estimated by means of elemental analysis and potentiometric titration.

Kinetic Measurements. The decarboxylation of the substrate, S, was initiated at 30°C by the addition of a solution of 0.6 mmol of S in 1 ml of ethanol to 99 ml of a buffer solution (pH = 9.0 with 0.025 M borate, $\mu = 0.035$) containing 0.12 meq of a cationic polymer. The progress of the reaction was followed spectrophotometrically at 410 nm (2-cyano-5-nitrophenolate, P, $\epsilon = 2.9 \times 10^3$) by using a Hitachi 124 spectrophotometer. In the case of a heterogeneous system, aliquots of the reaction mixture were quickly filtered and measured at desired time intervals.

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