of amineborane on the neutral or protonated carbonyl compound with the latter being favored. Possibly the reaction with amineborane is enhanced by factors, such as protonation, which increase the electron-deficient character of the carbonyl carbon atom.[15] These suggestions, however, are strictly speculative at this time. It should be noted that the reactions described herein proceed with the evolution of $H_2$ gas and therefore differ in stoichiometry from the reported reduction of monofunctional carbonyl compounds, such as acetone, with sodium borohydride. Factors influencing the stoichiometry of these reactions are being investigated, as are isotope and substituent effects on rates.

The high kinetic stability of these amineboranes suggests that they may become quite useful as hydridic reagents in aqueous acid. Although certain reductions proceed slowly in neutral or alkaline solution, the effect of acid in enhancing reaction rates provides a means for extensive practical use of amineboranes in the reduction of carbonyl compounds in water and mixed aqueous solvents.

**Acknowledgment.**—The authors wish to thank Mr. A. A. Hinckley for helpful discussions.

(15) Attack by amineborane at an electron-deficient center has been proposed to explain the increase in rate of reduction of cyclohexanone by various amineboranes in tetrahydrofuran with added $H_2SO_4$ or anhydrous HCl: see L. Murray. Ph.D. Thesis. Purdue University. Jan., 1963.

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### Selective Catalysis Involving Reversible Association of a Synthetic Polymeric Catalyst and Substrate[1]

*Sir:*

The high degree of substrate specificity exhibited by many enzymes is attributable, in part at least, to a specific binding of the substrate to the enzyme. Attempts to develop homogeneous systems of synthetic substances which exhibit selective catalytic features similar to those characterizing the enzymatic systems have met with only limited success. The best examples appear to be the solvolysis of substituted nitrophenyl acetates catalyzed by partially protonated poly(4-vinylpyridine),[2] poly(N-vinylimidazole),[2] and poly(4(5)-vinylimidazole).[3] In these cases substrates bearing a negatively charged substituent group exhibited unusually high reactivity, presumably as a consequence of electrostatic attraction between the substrate and catalyst.[4]

We now report results of an investigation of the solvolysis of copoly(acrylic acid-2,4-dinitrophenyl *p*-vinylbenzoate) (I) catalyzed by partially protonated

(1) This research was supported by the National Science Foundation. It benefitted also from a Public Health Service training grant (5T1-GM-626) from the National Institute of General Medical Science. Public Health Service.

(2) R. L. Letsinger and T. J. Savereide. *J. Am. Chem. Soc.*, **84**, 114 (1962); **84**, 3122 (1962).

(3) C. G. Overberger. T. St. Pierre. N. Vorchheimer, and S. Yaroslavsky. *ibid.*, **85**, 3413 (1963).

(4) In addition, H. Morawetz and J. A. Shafer. *Biopolymers*, **1**, 71 (1963). have described a case in which reactivity of a cationic ester is reduced as a result of association with a polyanion.
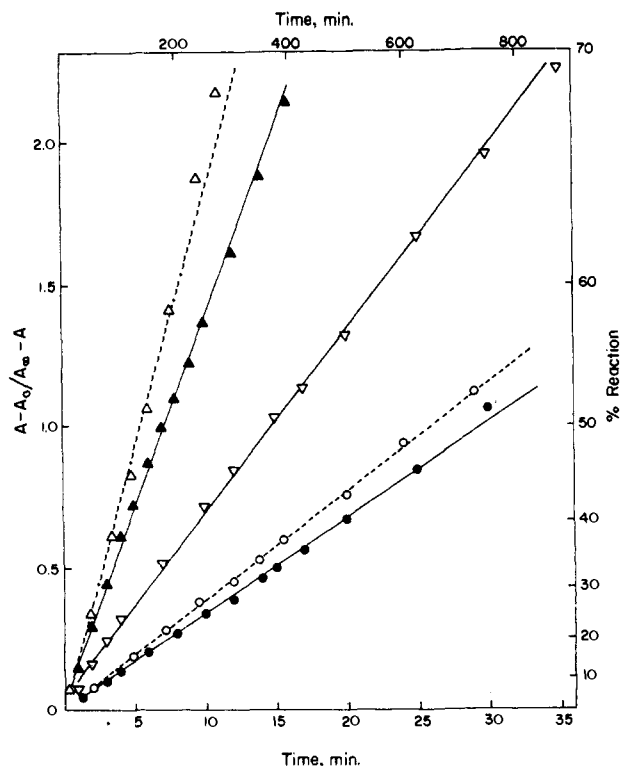
poly(N-vinylimidazole).[5] This polymer system exhibits a number of features of enzymatic reactions not found with the synthetic substances previously studied[2,3] and provides kinetic evidence for association of the catalyst with the substrate.



I



II
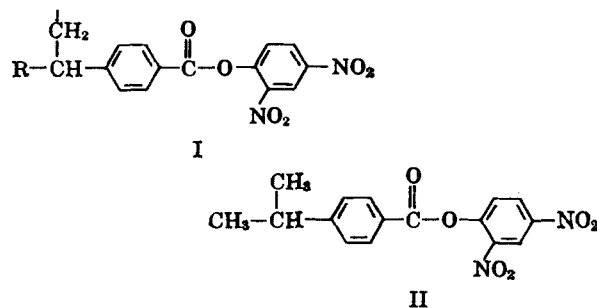
R contains $-CH_2CH-COOH$

Copolymer I ($\eta$ 0.09; 62% by weight dinitrophenyl vinylbenzoate) was prepared by polymerizing acrylic acid and 2,4-dinitrophenyl *p*-vinylbenzoate in benzene. Solvolyses were conducted in 50% (w./w.) ethanol-water at pH 7.5[6] and 25.0 ± 0.1° in a cuvette in a Beckman DU spectrophotometer, formation of 2,4-dinitrophenol being followed by the increase in absorbance at 412 m$\mu$.

Satisfactory pseudo-first-order kinetics were obtained for 2,4-dinitrophenyl *p*-isopropylbenzoate; however, curvature in the plots of log $(A_\infty - A)$ vs. time for the reaction of copolymer I was found.[7] In treating the data for I it was convenient to use the empirical relation[8]

$$(A - A_0)/(A_\infty - A) = k't$$

As shown in Fig. 1, a reasonably good fit to this equation was obtained for solvolyses conducted in the absence of active nucleophilic catalysts as well as in those catalyzed by N-methylimidazole and poly(N-vinylimidazole).

Rate data for a series of reactions in which the catalyst concentration was varied are presented in Fig. 2. With polyvinylimidazole good activity was found when the imidazole unit concentration was low ($5 \times 10^{-4}$ M). Moreover, the rate attained a limiting value at high catalyst concentrations. For experiments in which the concentration of copolymer I was varied, a plot of the rate, $(k' - k'_{\text{solvent}})$(initial concentration of ester groups), as a function of the initial ester concentration afforded a similarly shaped curve (Fig. 3). Both results are explicable on the basis that copolymer I and poly(N-vinylimidazole) associate in solution and that catalysis is highly efficient in the complex that is pro-

(5) Polyvinylimidazole was supplied by the Badische Anilin und Soda Fabrik. Ludwigshafen A. Rhein. Germany.

(6) This value was selected since clear solutions, free of turbidity, were obtained on mixing the polymeric substrate and catalyst (turbidity developed on mixing at pH 7 or lower) and the pH–rate profile exhibited a maximum at this value. All solutions were 0.01 M in potassium chloride and 0.02 M in 2,4,6-trimethylpyridine. That the spectral change was due to solvolysis was shown by repeatedly scanning the spectrum from 290 to 400 m$\mu$ in a Cary spectrophotometer as the reaction proceeded. The final spectrum was that of 2,4-dinitrophenol, and an isosbestic point occurred at 313 m$\mu$.

(7) Observation of complex kinetics in hydrolysis of functional groups on polymer chains is not uncommon. See. for example, J. Moens and G. Smets. *J. Polymer Sci.*, **23**, 931 (1957). and E. Gaetjens and H. Morawetz. *J. Am. Chem. Soc.*, **83**, 1738 (1961).

(8) "$k$" may be considered to be a pseudo-first-order rate constant defined by the expression $-dC/dt = k'C(C/C_0)$. where $C/C_0$ represents the relative reactivity of the ester groups on a polymer chain as a function of extent of reaction.

Fig. 1.—Solvolysis of copolymer I (6.14 $M$ in ester groups): —O—. without catalyst; —●—. with 0.02 $M$ N-methylimidazole; —Δ—. with 2.5 × 10⁻⁵ $M$ (concentration expressed in imidazole units) poly(N-vinylimidazole); —∇—, with 5 × 10⁻⁴ $M$ poly-(N-vinylimidazole); —▲—, with 0.02 $M$ poly(N-vinylimidazole). Solid lines. read bottom time scale; broken lines, read top time scale.

duced. The polymeric catalyst–substrate system is particularly favorable for demonstrating these phenomena since the individual substrate molecules possess numerous anionic sites that are attracted by the multiple cationic sites on the catalyst.

In support of the concept that reversible association between catalyst and substrate is involved in these reactions it was found that poly(acrylic acid), which competes with the copolymer for binding sites on poly-(N-vinylimidazole), functioned as an inhibitor in the catalyzed solvolyses (Table I).

TABLE I[a]

| Poly(acrylic acid) (moles/1. of ester groups) | $10^3 k'$. min.⁻¹ |
|---|---|
| 0 | 65 |
| 5 × 10⁻⁴ | 28[b] |
| 10 × 10⁻⁴ | 14[b] |

[a] Copolymer I, 6.4 × 10⁻⁵ $M$ in ester groups; poly(N-vinyl-imidazole), 5 × 10⁻⁴ $M$ in imidazole units. [b] $k'$ decreased somewhat as the reaction progressed. These values correspond to the first 30% of the reaction.

TABLE II

| Catalyst | $10^3 k$. min.⁻¹ (dinitrophenyl isopropylbenzoate) | $10^3 k$. min.⁻¹ (copolymer I) |
|---|---|---|
| None | 2.2 | 1.54 |
| N-Methylimidazole (2 × 10⁻² $M$) | 56.5 | 33. |
| Polyvinylimidazole (5 × 10⁻⁴ $M$ in imidazole units) | 3.1 | 65 |

Data demonstrating selective solvolysis of a pair of substituted dinitrophenyl benzoates are given in Table II. With N-methylimidazole as catalyst 2,4-dinitro-
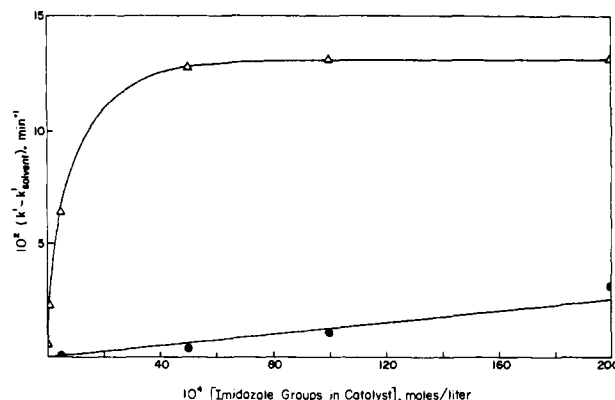


Fig. 2.—Solvolysis of copolymer I (6.14 × 10⁻⁴ $M$ in ester groups) catalyzed by poly(N-vinylimidazole) (—Δ—), 2.5 × 10⁻⁵—2 × 10⁻² $M$ in imidazole groups, and by N-methylimidazole (—●—), 5 × 10⁻⁴—2 × 10⁻² $M$.
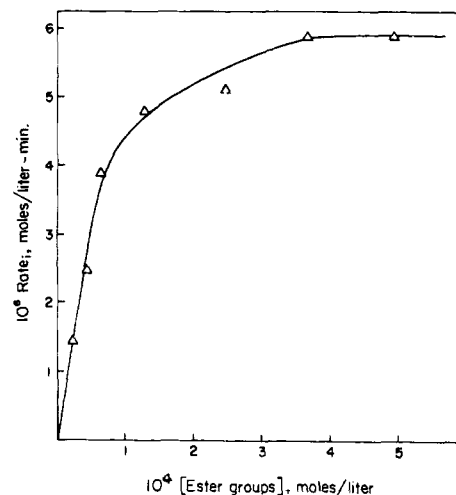


Fig. 3.—Solvolysis of copolymer I, catalyzed by poly(N-vinyl-imidazole. 5 × 10⁻⁴ $M$.

phenyl $p$-isopropylbenzoate solvolyzed somewhat faster than copolymer I. On changing the catalyst to poly(N-vinylimidazole) it was found that copolymer I solvolyzed markedly faster than dinitrophenyl $p$-isopropylbenzoate. Selectivity results from *acceleration* in the rate of solvolysis of the substrate capable of binding to the catalyst.

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## The Effect of Electrolytes on Circular Dichroism Curves of [Co(en)₃]Cl₃

Sir:

It is well known that the observed optical rotation of optically active complexes depends upon the optically inactive ions present as charge compensators. Some previous studies of this effect have been carried out either at a fixed concentration of inactive ion,[1] or at only one wave length.[2] Tsuchida[3] has reported that the maximum in the optical rotatory dispersion (ORD)

(1) M. J. Albinak, D. C. Bhatnagar, S. Kirschner, and A. J. Sonnessa. Can. J. Chem., 39, 2360 (1961).
(2) R. Larsson, Acta Chem. Scand., 16. 2267 (1962).
(3) R. Tsuchida, J. Chem. Soc. Japan, Pure Chem. Sect., 58. 621 (1937).