AIBN were then added. In general, the tubes were degassed at 10^{-5}–10^{-6} mm with three successive freeze–thaw cycles before sealing under vacuum. In several cases the reactions were run under a cover of nitrogen, warming the reaction mixtures to the temperature under study before the addition of the initiator. After 2 hr the reaction mixtures were cooled to room temperature, opened under a cover of nitrogen, and sealed with a serum stopper before being analyzed by glpc. Analyses were performed on aluminum 4–7 ft × 0.25 in. 20% SE-30 on 60–80 Chromosorb W, reg columns. Quantitative measurements were made with the use of appropriate internal standards and sensitivity corrections.

Acknowledgment. This work was supported by grants from the Petroleum Research Fund (2439-AC4), administered by the American Chemical Society, and the National Cancer Institute of the Public Health Service (CA 11045).

Catalytic Action of Polyelectrolytes on the Alkaline Fading Reactions of Triphenylmethane Dyes[1]

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Abstract: The alkaline fading reactions of crystal violet (CV), ethyl violet (EV), malachite green (MG), and brilliant green (BG) in aqueous solutions (reactions between oppositely charged ionic species) were studied in the presence of cationic and anionic polyelectrolytes and surfactants. The polymer catalysts examined are poly(4-vinylpyridine) quaternized with alkyl halide (C_nPVP) [alkyl = ethyl ($n = 2$), *n*-propyl (3), *n*-butyl (4), and cetyl 16)] and with benzyl halide (BzPVP), copolymer of diethyldiallylammonium chloride and sulfur dioxide (DECS), sodium poly(ethylene sulfonate) (NaPES), sodium poly(styrene sulfonate) (NaPSS), sodium polyacrylate (NaPAA), and NaDNA. Surfactants used are cetyltrimethylammonium bromide and sodium lauryl sulfate. The fading reactions of CV, EV, MG, and BG are *accelerated* by the cationic polyelectrolytes having hydrophobic groups. The largest acceleration factor observed is $\sim 10^2$ for the EV–CTABr system, and the strength of the acceleration is in the order: $C_2PVP < C_3PVP < C_4PVP < BzPVP < C_{16}BzPVP$. By the addition of anionic polyelectrolyte, on the other hand, the fading reaction is *retarded* with the largest deceleration factor of 10^4 for the EV–NaPSS system, and the order of the retarding efficiency is NaPES $\sim$ NaPAA $\ll$ NaDNA $<$ NaPSS. The acceleration and deceleration factors caused by the catalysts are largest for EV and smallest for MG with the order: MG $<$ BG $<$ CV $<$ EV. These results suggest the important contribution of the hydrophobic interactions between the dye and the polymer catalyst. The acceleration by the hydrophobic cationic polymer is due to the enthalpic loss, whereas the deceleration by the hydrophobic anionic polymer is due to a decrease of entropy. The fading of phenolphthalein (PP) (reaction between ionic species with charges of the same sign) is not influenced by anionic polymers, whereas it is accelerated by cationic polymers having small hydrophobic groups and decelerated strongly by highly hydrophobic cationic polymers.

Recently, there appeared a large number of publications dealing with organic and inorganic reactions in the presence of polyelectrolytes.[2] In our laboratory, catalytic action of polyelectrolytes on interionic reactions has been studied in order to understand the nonspecific, general aspect of the polymer catalyses.[3-9] Other types of interactions, such as hydrophobic, hydrogen-bonding, and charge-transfer interactions between ionic reactant and catalyst, however, are easily understood to be also important and can be even more so under some circumstances than electrostatic ones. The purpose of the present work is mainly to discuss the comparative strength of contributions of various interactions between a substrate and a polymer catalyst. The relative strength of the hydrophobic interactions in comparison with the electrostatic ones will be considered. The principal contribution of the hydrophobic interactions between substrate and catalyst in interionic reactions was demonstrated first by Grunwald, *et al.*,[10-12] and quite recently by Cordes, *et al.*,[13] for alkaline fading reactions of triphenylmethane dyes in the presence of detergents. A similar conclusion was reached by Sakurada for a series of hydrolysis reactions of various esters in the presence of polysulfonic acid.[14] The triphenylmethane dye is a hydrophobic ionic substrate, and the fading reactions of the dye with hydroxide ion have been

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[1] Presented at the 20th Symposium of Polymer Science, Tokyo, Japan, Nov 1971. The term "catalytic action of polyelectrolyte" is used throughout the present paper in the customary fashion. However, we do not imply that the polyelectrolytes are really catalysts as defined earlier by W. Ostwald, *Phys. Z.*, 3, 313 (1902).

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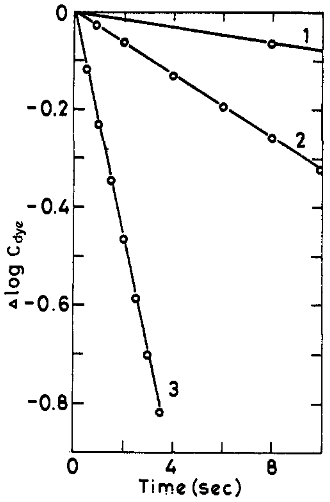

Figure 1. First-order plot for the fading reaction of BG at 25° ([BG] = 1.25×10^{-5} *M*, [OH$^-$] = 3.49×10^{-2} *M*): (1) no added salt, (2) $\mathrm{C_{16}}$BzPVP (3.49×10^{-3} equiv l.$^{-1}$), (3) CTABr (1.16×10^{-3} *M*).

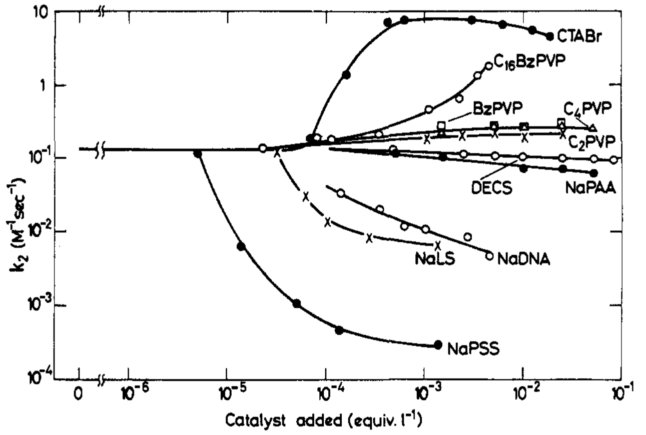

Figure 2. Catalytic action of polyelectrolytes on the fading reaction of EV at 30° ([EV] = 1.05×10^{-5} *M*, [OH$^-$] = 1.05×10^{-2} *M*).

thoroughly studied by many investigators.[15–20] Thus, these reactions were thought to be interesting for further study of the polyelectrolyte catalysis in ionic reactions.

Experimental Section

Materials. **Poly(4-vinylpyridine)** was prepared at 45° by bulk polymerization of 700 ml of 4-vinylpyridine (bp 56° (11 mm)) with 2.0 g of benzoyl peroxide.[21] The polymerization mixture was agitated vigorously for 4 hr. Clear and light amber viscous liquid was obtained and then poured into toluene (40 l.). The polymer product thus obtained was washed with toluene for 3 hr and dried under vacuum at 40°. A white threadlike product (600 g) was obtained; the degree of polymerization was estimated to be 3800 by viscometry.[22]

Anal. Calcd for n-$\mathrm{C_7H_7N}$: C, 80.0; H, 6.7; N, 13.3. Found: C, 80.3; H, 6.5; N, 13.3.

Poly(4-vinyl-*N*-ethylpyridinium bromide) ($\mathrm{C_2}$PVP) was prepared by heating 150 ml of ethyl bromide and 10.4 g of poly(4-vinylpyridine) in 100 ml of nitromethane for 3 days at 45°. The product was recovered by vacuum evaporation and was dissolved in 200 ml of 95% ethanol; the solution was poured into 2 l. of dioxane. A granular hygroscopic white powder was obtained by drying the precipitate thus obtained under vacuum (80% in yield). The degree of quaternization was 0.96 from elemental analysis and conductometric determination of Br$^-$ with $\mathrm{AgNO_3}$.

Anal. Calcd for n-$\mathrm{C_9H_{12}NBr}$: C, 50.5; H, 5.7; N, 6.5; Br, 37.3. Found: C, 48.4; H, 5.9; N, 6.0; Br, 36.5.

Poly(4-vinyl-*N*-propylpyridinium bromide) ($\mathrm{C_3}$PVP) was obtained from n-propyl bromide (120 ml) and poly(4-vinylpyridine) (10.4 g) in 180 ml of nitromethane. The same conditions as those used above for $\mathrm{C_2}$PVP were used (yield 80%). The degree of quaternization was 0.95. *Anal.* Calcd for n-$\mathrm{C_{10}H_{14}NBr}$: C, 52.6; H, 6.1; N, 6.1; Br, 35.1. Found: C, 52.1; H, 6.3; N, 5.8; Br, 33.8.

Poly(4-vinyl-*N*-butylpyridinium bromide) ($\mathrm{C_4}$PVP) was synthesized according to the method of Fuoss and Strauss[23] from n-butyl bromide and poly(4-vinylpyridine) in nitromethane. The degree of quaternization was 0.95. *Anal.* Calcd for n-$\mathrm{C_{11}H_{16}NBr}$: C, 54.6; H, 6.6; N, 5.8; Br, 33.1. Found: C, 52.6; H, 7.2; N, 5.3; Br, 32.1.

Poly(4-vinyl-*N*-benzylpyridinium chloride) (BzPVP) was prepared by addition of benzyl chloride (100 ml) to the solution of poly(4-vinylpyridine) (10.4 g) in nitromethane (200 ml). The quaternization was carried out at 45° for 3 days. The solvent and the excess of benzyl chloride were eliminated by vacuum evaporation. The product was dissolved in ethanol and precipitated in dioxane. A white hygroscopic powder was obtained by centrifugation of the dioxane solution and drying the precipitate under vacuum (70% in yield). The degree of quaternization of the product was 0.92. *Anal.* Calcd for n-$\mathrm{C_{14}H_{14}NCl}$: C, 72.2; H, 6.5; N, 6.0; Cl, 15.2. Found: C, 69.0; H, 6.4; N, 5.7; Cl, 14.5.

Copolymer of 4-Vinyl-*N*-benzylpyridinium Chloride and 4-Vinyl-*n*-cetylpyridinium Bromide ($\mathrm{C_{16}}$BzPVP). This polymer was prepared by a method similar to that described by Strauss and Gershfeld[24] for the preparation of a copolymer of 4-vinyl-*N*-ethylpyridinium bromide and 4-vinyl-*N*-*n*-dodecylpyridinium bromide. An intermediate polymer, poly(4-vinylpyridine), partially quaternized with n-hexadecyl bromide, was prepared from 20 g of poly(4-vinylpyridine) dissolved in 160 ml of a 1:1 nitromethane–nitroethane mixture and 50 ml of n-hexadecyl bromide. The reaction was allowed to proceed for 3 hr at 45°. The reaction mixture was poured into ethyl acetate at 0°. *Anal.* Found (intermediate polymer): C, 77.4; H, 7.4; N, 11.5; Br, 3.3. The degree of quaternization with $\mathrm{C_{16}H_{33}Br}$ was estimated to be 0.05. $\mathrm{C_{16}}$BzPVP was prepared by refluxing the intermediate polymer with benzyl chloride in nitromethane at 45° for 3 days. The reaction mixture was poured into ethyl acetate at 0°, and the precipitate was purified by the precipitation from ethanol into ethyl acetate. The total degree of quaternization was 0.97. *Anal.* Found for final product, (m-$\mathrm{C_{14}H_{14}NCl}\cdot n$-$\mathrm{C_{23}H_{40}NBr}$): C, 70.1; H, 6.6; N, 5.6.

Sodium poly(styrene sulfonate) (NaPSS) was a gift from the Dow Chemical Co., Midland, Mich. The degree of polymerization was 2500. Sodium poly(ethylene sulfonate) (NaPES), degree of polymerization 770, was kindly donated by the Hercules Powder Co., Wilmington, Del. Sodium polyacrylate (NaPAA) was furnished by the Toa Gosei Chemicals Co., Nagoya, Japan. The weight-average degree of polymerization was 640. Dilute solutions of these three anionic polyelectrolytes were converted to the acid form by passing them through columns of cation- and anion-exchange resins. Completeness of the conversion was assured by the measurement of sodium atom by an atomic absorption spectrophotometer. The corresponding sodium salts were prepared by neutralization with aqueous solutions of sodium hydroxide.

The sodium salt of salmon sperm DNA (NaDNA) employed in the present investigation was purchased from Calbiochem Corp., Los Angeles, Calif. The material was washed with 85% ethanol (the pH was adjusted to ~7–8 by adding 0.001 *N* NaOH), then with pure ethanol, and further with pure acetone. Then the NaDNA was dried for 1 day under vacuum. The denaturation of NaDNA was accomplished by heating its solution for 10 min at 90° and cool-

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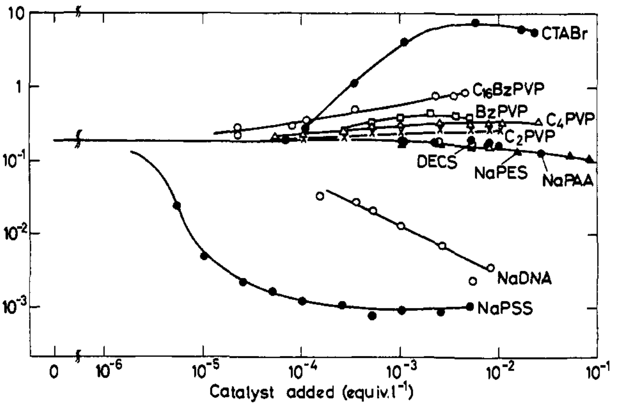

Figure 3. Catalytic action of polyelectrolytes on the fading reaction of CV at 30° ([CV] = 1.05×10^{-5} *M*, [OH^-] = 1.05×10^{-2} *M*).

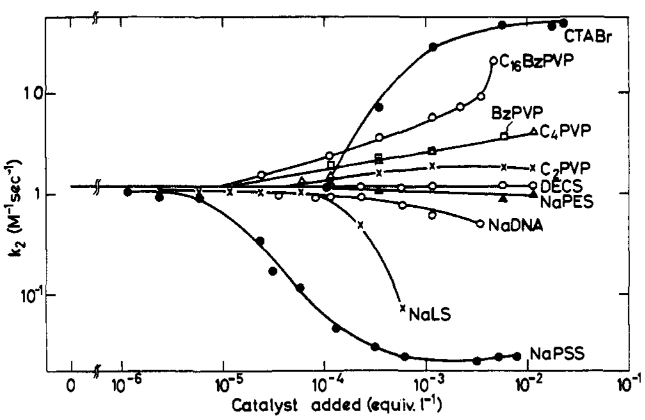

Figure 4. Catalytic action of polyelectrolytes on the fading reaction of BG at 30° ([BG] = 1.25×10^{-5} *M*, [OH^-] = 3.49×10^{-2} *M*).

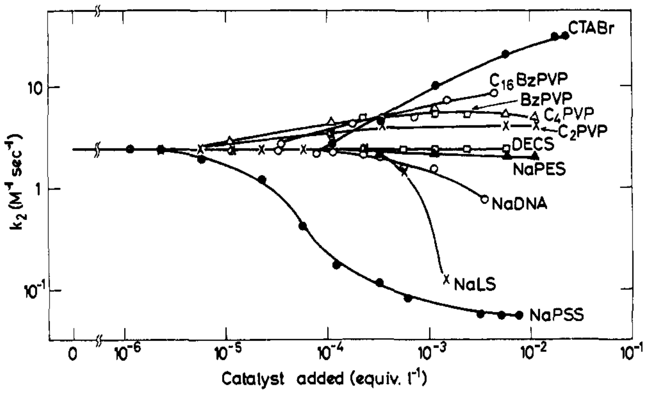

Figure 5. Catalytic action of polyelectrolytes on the fading reaction of MG at 30° ([MG] = 1.25×10^{-5} *M*, [OH^-] = 3.49×10^{-2} *M*).

ing rapidly in ice. The denaturation was checked by the hypochromism at 260 nm.

The copolymer of diethyldiallylammonium chloride and sulfur dioxide (DECS) is a strongly basic polyelectrolyte found by Harada, *et al.*[25,26] Sodium lauryl sulfate (NaLS) and cetyltrimethylammonium bromide (CTABr) were commercially available guaranteed reagents. Crystal violet (CV), ethyl violet (EV), malachite green (MG), brilliant green (BG), and phenolphthalein (PP) of Merck (grade for microscopy or bacteriology) were used without further purification. Aqueous solutions of sodium hydroxide were used within 1 week after preparation. Deionized water was distilled under a nitrogen atmosphere for the preparation of the solutions of substrate and polymer catalyst.

Kinetic Measurements. Catalyst solutions were prepared in water containing a certain amount of sodium hydroxide, and substrate solutions were prepared in pure water. The reaction was started by mixing the catalyst solution with the substrate solution. The concentrations of both catalyst and substrate were determined gravimetrically. The dyes used in the present investigation have been found to obey Beer's law up to a concentration of 10^{-5} *M*.[27-29] The reaction was, therefore, followed by observing the change in absorbance with time at dye concentrations lower than 10^{-5} *M*. The reaction velocity was monitored by measuring the absorption at 600 nm (for CV and EV) and 550 nm (for PP) by using a Hitachi spectrophotometer Model EPS-3T. For rapid fading reactions of MG and BG, the kinetic studies were performed with a Hitachi stopped-flow spectrophotometer, Model RSP-2. Changes of absorbance at 620 nm with time were recorded on a Hitachi storage oscilloscope, Model V-018. The strongly retarded fading reaction of MG and BG was, however, monitored by the EPS-3T spectrophotometer.

Results and Discussion

In the initial stages, the fading reactions followed first-order kinetics. In Figure 1, for example, the first-order plots for the fading of BG obtained by the stopped-flow spectrophotometer are shown. Since the concentration of OH^- is much higher than the concentration of the dye, a second-order rate constant, k_2, is defined by $k_2 = k_1/c_{OH^-}$. The changes of the equilibrium constant with addition of polyelectrolyte did not affect the k_2 value within experimental error.

In Figures 2–5, k_2 is shown for the fading reactions of EV, CV, BG, and MG as a function of the concentration of various polyelectrolytes. Both accelerations and decelerations were observed. A cationic micelle, CTABr, accelerated the reaction as was found earlier by Grunwald, *et al.*[10-12] Strongly basic polymers, *i.e.*, poly(4-vinylpyridine) quaternized with alkyl bromides, also accelerated the fading reaction, and the larger the alkyl group the larger the acceleration. This acceleration by highly charged polymers or particles is particularly noteworthy since the ammonium cyanate–urea conversion, which is also a reaction between oppositely charged ionic species, has been found to be decelerated.[6] The present experimental results imply that the hydrophobic *attractive* forces between the dye and the catalyst polymer predominate over the electrostatic *repulsive* forces. Both the dye ions and hydroxyl ions can, therefore, be accumulated around the polymer catalyst, and the reaction is facilitated. On the other hand, the cationic polyelectrolyte DECS, which is not so strongly hydrophobic, repels the dye ions and therefore decelerates the fading reaction as seen from Figures 2 to 5. This is reasonable because only an electrostatic action is important in this case. The difference in the catalytic actions between the polymeric pyridinium salts and DECS clearly shows the marked contribution of the hydrophobic forces.

We note that the catalytic influence of the cationic polyelectrolytes is in the order DECS < C_2PVP < C_3PVP < C_4PVP < BzPVP < C_{16}BzPVP as seen from Figures 2 to 5.

The fading reaction of the dyes was retarded by the

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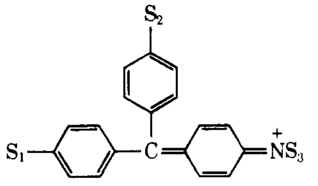
addition of anionic polyelectrolytes, *i.e.*, NaPAA, NaDNA, and NaPSS (see Figures 2–5). The retarding action of NaLS was also shown for comparison. The order of the retarding strength is NaPES $\sim$ NaPAA $\ll$ NaDNA $<$ NaPSS. By the addition of the anionic polyelectrolytes, the dye cations can be attracted to the vicinity of the polyanions, whereas the other reactant, OH^-, is repelled by electrostatic interaction. NaPAA and NaPES are known not to be hydrophobic,[29,30] whereas NaPSS is strikingly hydrophobic.[30–32] The sequence of retardation efficiency may indicate the order of the hydrophobicity of the polymer.

NaDNA strongly decelerated the reaction, which indicates the strong hydrophobic nature of the DNA molecule. This is consistent with the results of other investigations.[33,34]

The acceleration and/or deceleration factors of the catalyst examined are the largest for EV. The ratio of the highest rate in the presence of CTABr to the lowest one in the presence of NaPSS amounts to $\sim 10^4$–10^5. The ratio for MG is about 10^3. For all the substrates investigated, we have MG $<$ BG $<$ CV $<$ EV. This order reflects the hydrophobicity of the dye. The number of methylene groups of the substituents of the dye is largest for EV and decreases in the above order, except for the CV–BG sequence as shown in Table I. The reversal of the CV–BG sequence may be due to the difference of the concentrations of OH^-, *i.e.*, 1.05×10^{-2} and 3.49×10^{-2} *M* for CV and BG, respectively, since the catalytic action increases with a decreasing concentration of OH^-.

Table I. The Structure of EV, CV, BG, and MG



Triphenylmethane dye

Dye	S_1	S_2	S_3	Total no.[a]
EV	$N(C_2H_5)_2$	$N(C_2H_5)_2$	$(C_2H_5)_2$	12
CV	$N(CH_3)_2$	$N(CH_3)_2$	$(CH_3)_2$	6
BG	H	$N(C_2H_5)_2$	$(C_2H_5)_2$	8
MG	H	$N(CH_3)_2$	$(CH_3)_2$	4

[a] Of methyl and methylene groups of $S_1 + S_2 + S_3$.

The accelerating and decelerating actions of the polymer catalysts are observable even at extreme dilution, *i.e.*, $\sim 10^{-6}$–10^{-5} equiv l.$^{-1}$, whereas the surfactants act as efficient catalysts only in more concentrated solutions (Figures 2–5). This is due to the simple fact that surfactants such as CTABr and NaLS form micelle structures only above the critical micelle concentration.

The fading reactions of BG in aqueous media were studied in a temperature range 20–40° at a dye concentration of 1.25×10^{-5} *M* and an alkali concentration of 3.49×10^{-2} *M*. The plot of log k_2 *vs.* $1/T$ gave a straight line. The activation parameters are tabulated in Table II. The $\Delta S^{\ddagger}$ value was negative in the absence of added salt which is in contradiction with positive values usually found for interionic reactions between ionic species of opposite charge. The negative values of $\Delta S^{\ddagger}$ were, however, often observed in dye fading reactions.[17–20] As is shown in Table II, $\Delta G^{\ddagger}$ decreased by cationic polyelectrolyte (C_{16}BzPVP) or cationic surfactant (CTABr), and increased by anionic polymer (NaPSS) or detergent (NaLS), which reflects the acceleration and deceleration effects of these salts, respectively. The $\Delta H^{\ddagger}$ value was decreased both by cationic and anionic catalysts, as has been found for interionic reactions catalyzed with a polyelectrolyte.[2–6] The $\Delta S^{\ddagger}$ value decreased on addition of the anionic salts, *i.e.*, NaPSS and NaLS, whereas it was rather insensitive toward cationic catalysts, such as C_{16}BzPVP and CTABr (Table II). In other words, the acceleration with the hydrophobic cationic catalysts resulted from a negative enthalpic change, while the deceleration by polyanions or anionic detergents was entropic. The latter is consistent with previous data on the catalysis of the ammonium cyanate–urea conversion by polyelectrolytes.[6]

Table II. Activation Parameters for the Fading Reaction of BG at 30°[a]

Added salt	Concn of salt, equiv l.$^{-1}$	$\Delta G^{\ddagger}$, kcal mol^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}
None	0	17.8	8.8	−30
C_{16}BzPVP	3.49×10^{-3}	17.0	7.2	−32
CTABr	1.16×10^{-3}	15.8	7.9	−26
NaPSS	5.81×10^{-5}	19.4	8.3	−37
NaLS	5.81×10^{-4}	19.6	7.4	−40

[a] [BG] = 1.25×10^{-5} *M*, [OH^-] = 3.49×10^{-2} *M*.

Next, we discuss the catalysis by polyelectrolytes of the alkaline fading of PP. Since the valency of phenolphthalein is −2 in the alkaline region, the fading reaction involves two negatively charged species. The experimental results are listed in Tables III and IV.

Table III. Catalytic Action of Polyelectrolyte on the Alkaline Fading Reaction of Phenolphthalein at 25°[a]

Catalyst[b]	k_2, M^{-1} sec^{-1}	Initial absorbance at 553 nm
None	0.0050	1.175
DECS	0.058	0.694
C_2PVP	0.096	0.492
C_3PVP	0.080	0.388
C_4PVP	0.051	0.287
BzPVP		0.350

[a] [PP] = 4.21×10^{-5} *M*, [NaOH] = 1.05×10^{-2} *M*. [b] [Polymer] = 2.63×10^{-4} equiv l.$^{-1}$.

The polycations accelerated the reaction, whereas the polyanions had no effect on the reaction rate. As the hydrophobicity of polycations was increased, the degree of acceleration increased, passed a maximum, and then decreased. By the addition of BzPVP, the fading reaction was strongly hindered and was stopped nearly completely at a BzPVP concentration of 1.05 ×

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Table IV. Effect of Polyelectrolyte on the Alkaline Fading Reaction of Phenolphthalein at 25°[a]

Catalyst	Concn of catalyst, equiv l.$^{-1}$	k_2, M^{-1} sec^{-1}	Initial absorbance at 553 nm
None	0	0.015	1.175
DECS	5.26×10^{-5}	0.018	1.116
	2.63×10^{-4}	0.024	1.023
	1.05×10^{-3}	0.041	0.857
C_2PVP	5.26×10^{-5}	0.020	1.076
	2.63×10^{-4}	0.037	0.836
	1.05×10^{-3}	0.081	0.466
C_3PVP	5.26×10^{-5}	0.017	1.097
	2.63×10^{-4}	0.021	0.857
C_4PVP	5.26×10^{-5}	0.017	1.053
	2.63×10^{-4}	0.017	0.720
BzPVP	5.26×10^{-5}	0.015	1.066
	2.63×10^{-4}	0.0064	0.707
	1.05×10^{-3}	0	0.315
NaPSS	1.05×10^{-3}	0.015	1.172
	7.90×10^{-3}	0.015	1.197

[a] [PP] = 4.21×10^{-5} *M*, [NaOH] = 1.05×10^{-1} *M*.

10^{-3} equiv l.$^{-1}$ (Table IV). Here, presumably, the attractive forces between the indicator and the catalyst are so strong as a result of both electrostatic and hydrophobic interactions that the attack of the hydroxyl ions on the indicator is sterically hindered. Similar effects of a hydrophobic polymer catalyst have been reported on a reaction between two ions with charges of the same sign.[35]

The last columns of Tables III and IV give the change of the initial absorbance at 553 nm, the maximum peak of PP. The red or blue shift of the peak could not be observed by the addition of catalyst. Kinetic data were practically independent of such changes in the initial absorbance at 553 nm. As is seen in the tables, the larger the catalytic action of the macrocation, the larger the decrease of the absorbance. The reverse does not, however, necessarily hold, since by the addition of strongly hydrophobic macrocation (*e.g.*, BzPVP), the absorbance decreased drastically, but the reaction was largely repressed. We may regard the decrease in the absorbance as a measure of the binding strength of the indicator with the catalyst.

Acknowledgment. The Hitachi stopped-flow spectrophotometer Model RSP-2 was purchased by a grant administered by the Ministry of Education.

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Differentiation of 1,4- and 1,5-Disubstituted Imidazoles[1]

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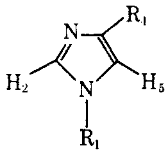
Received October 10, 1972

Abstract: A method is presented for distinguishing 1,4- and 1,5-disubstituted imidazoles by their proton cross-ring coupling constants. Other spectral methods also have been evaluated, as well as several methods which have been reported for differentiating such isomers. Comparison of these methods leads to the conclusion that the measurement of cross-ring coupling constants is the most generally satisfactory and reliable procedure. On this basis, structures are assigned to the carboxymethylhistidines, and the histamine metabolite is established as 1-β-D-ribofuranosyl-4-imidazoleacetic acid.

The considerable biological importance of the group of compounds incorporating the imidazole nucleus has stimulated much work on this heterocycle.[2] A remaining and important problem in this field has been the inability easily and reliably to differentiate 1,4- (I) and 1,5- (II) disubstituted imidazoles, either obtained from natural sources or prepared by ambiguous N-alkylation of the corresponding 4(5)-imidazoles. Isomer assignments have been made by analogy to similar reactions,[3] spectroscopic means,[4] conversion to known compounds,[5] or steric arguments.



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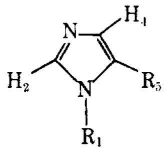

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