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Comparison of Biomimetic Catalytic Properties of Modified Polyethylenimines with Those of Micelles

IRVING M. KLOTZ, EVELYN N. DRAKE, AND MASAHIKO SISIDO

Department of Chemistry, Northwestern University, Evanston, Illinois 60201

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Polyethylenimine provides a remarkably versatile macromolecular matrix for the introduction of environments that might accelerate specific chemical reactions. Two features of the behavior of such modified polymers are described. (1) Alkylated cationic derivatives of polyethylenimine are effective in providing an environment for nucleophilic catalysis of hydrolysis of nitrophenyl acylates, much more so than are corresponding alkyl cationic micelle-forming detergents. (2) Donor–acceptor electron transfer can be influenced by preferential interactions of the macromolecule with radical ions; again the polymer is more effective than micelles. In general, apolar, quaternized polyethylenimines facilitate chemical changes that would otherwise not occur readily in aqueous solution.

INTRODUCTION

The elucidation of molecular pathways and mechanisms in enzyme-catalyzed reactions has progressed remarkably in the last two decades. As the structural details of active sites in enzyme macromolecules have been progressively revealed, it has become increasingly tantalizing to try to produce a synthetic macromolecule with local environments and functional groups that could catalyze specific chemical transformations. Such systems would serve to test the validity of concepts being used to interpret enzyme catalysis. Furthermore, they could lead to the production of novel macromolecular catalysts that might have practical applications.

Our major efforts in this direction have been with the macromolecular framework of polyethylenimine (*1*). This polymer provides a remarkably versatile matrix for the attachment of a wide variety of types of functional groups. These endow the polymer with different types of local environments which greatly increase the affinity of the polymer for small molecules and thereby set the stage for catalytic modifications. In this study, some comparisons in these regards have been made between quaternized polyethylenimines and analogous cationic micelles.

EXPERIMENTAL

PEI-600, a poly(ethylenimine) derivative with average molecular weight of about 60,000, was obtained from Dow Chemical Company as a 33% aqueous

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solution. For the electron-transfer studies, the polymer was ultrafiltered in an Amicon apparatus using a Diaflow PM-30 membrane. For all samples, water was removed from the polymer by rotary evaporation. Absolute ethanol was added to dissolve the polymer and then removed by rotary evaporation; this procedure was repeated for several successive cycles. It produces a polymer free of significant amounts of water (*2*).

Quaternization of polyethylenimine was carried out by procedures described previously (*3–5*). Lauryl groups were attached by alkylation with lauryl iodide or lauryl bromide. Quaternization of residual amine nitrogens was effected with methyl iodide and with dimethyl sulfate. The modified polymers prepared had the following stoichiometric compositions, where $m \simeq 1400$:

$$(C_2H_4N)_m(C_{12}H_{25})_{0.1m}(CH_3)_{1.9m} \quad \text{(I)}$$
$$(C_2H_4N)_m(C_{12}H_{25})_{0.25m}(CH_3)_{1.7m} \quad \text{(II)}$$
$$(C_2H_4N)_m(C_{12}H_{25})_{0.5m}(CH_3)_{1.5m} \quad \text{(III)}$$
$$(C_2H_4N)_m(C_{12}H_{25})_{0.25m}(CH_3)_{1.6m} \quad \text{(IV)}$$
$$(C_2H_4N)_m(CH_3)_{1.6m}. \quad \text{(V)}$$

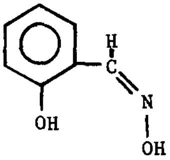
Dodecyltrimethylammonium chloride and hexadecyltrimethylammonium chloride (or bromide) were purchased from Eastman Organic Chemicals. Tetramethylphenylenediamine and chloranil were obtained from commercial sources; the former was sublimed before use and the latter was recrystallized from acetone. 3-Nitro-4-acetoxybenzoic acid was prepared according to the method of Overberger *et al.* (*6*), mp 150–152°C, lit. (*7*) 152°C. *p*-Nitrophenylcaproate and *p*-nitrophenyllaurate were obtained from Sigma Chemical Company and salicylaldoxime from Eastman. *p*-Nitrophenylacetate was a gift from Dr. Alice Tsai.

RESULTS AND DISCUSSION

Aldoxime-Nitrophenyl Ester Reactions

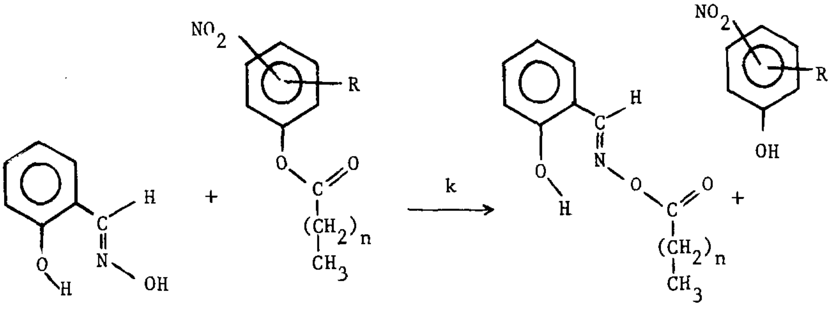
The polyethylenimines offer a very suitable matrix for nucleophilic moieties that have catalytic potential in hydrolytic reactions. Since the original discovery of the catalytic effects of the imidazole molecule per se (*8*, *9*), this residue has been widely used in the polymeric state (*10–13*) to accelerate hydrolytic reactions. Alternatively, the hydroxamate group, attached to polymers, has been tried as a nucleophilic polymer catalyst (*14*, *15*). Nevertheless, there is still much room for more effective nucleophiles.

An attractive alternative nucleophile is the aromatic salicylaldoxime, (VI).



(VI)

The intrinsic pK_a of this compound, about 9.5 (*16*), is substantially higher than that of imidazole, and hence (VI), in its anionic form, would be expected to be a nucleophile superior to imidazole. Furthermore, in the environment of polyethylenimines the pK_a of salicylaldoxime should be lowered substantially so that the concentration of effective component, the anion, should be increased in the pH range near 7. Catalytic effects of quaternized polyethylenimine derivatives (*3, 17*) have been evaluated here on the basis of their ability to catalyze the following reaction:



$$\mathrm{SA} + \mathrm{NPE} \xrightarrow{k} \mathrm{SAE} + \mathrm{NP} \qquad [1]$$

In the absence of polymer, rates of acylation of salicylaldoxime (SA) with nitrophenyl ester (NPE) were analyzed in terms of the following equation:

$$\frac{-d[\mathrm{NPE}]}{dt} = \frac{d[\mathrm{NP}]}{dt} = k[\mathrm{SA}][\mathrm{NPE}] + k'[\mathrm{H}^+][\mathrm{NPE}] + k''[\mathrm{OH}^-][\mathrm{NPE}] + k'''[\mathrm{H_2O}][\mathrm{NPE}]. \qquad [2]$$

Included in Eq. [2] are terms for the acid (k'), base (k''), and uncatalyzed (k''') hydrolysis of nitrophenyl ester in addition to the term for acylation of salicylaldoxime. These hydrolytic reactions contribute to the rate of appearance of nitrophenol in aqueous solutions containing nitrophenyl ester, and must be taken into account in determinations of k, the second-order rate constant for acylation of salicylaldoxime with nitrophenyl ester. At fixed pH, Eq. [2] can be simplified to

$$d[\mathrm{NP}]/dt = k[\mathrm{SA}][\mathrm{NPE}] + k_{\mathrm{bkg}}[\mathrm{NPE}], \qquad [3]$$

where

$$k_{\mathrm{bkg}} = k'[\mathrm{H}^+] + k''[\mathrm{OH}^-] + k'''[\mathrm{H_2O}]. \qquad [4]$$

From eq. [3] it can be seen that a plot of $d[\mathrm{NP}]/dt$ versus [SA] should give a straight line with slope equal to k[NPE].

Initial rates of appearance of nitrophenol, $d[\mathrm{NP}]/dt$, were determined in a series of reaction mixtures containing fixed initial concentrations of nitrophenyl ester and variable initial concentrations of salicylaldoxime. Linear least-squares analysis of $d[\mathrm{NP}]/dt$ vs [SA] yielded slopes which, when divided by the fixed initial concentration of nitrophenyl ester, gave the following values of k for the respective nitrophenylcarboxylates:

Nitrophenyl ester	k (liter mol^{-1} min^{-1})
p-Nitrophenylacetate	31.7
p-Nitrophenylcaproate	29.4
p-Nitrophenyllaurate	14.9
3-Nitro-4-acetoxybenzoic acid	10.8

Rates of oxime acylation in the presence of quaternized polyethylenimine derivatives were determined in the following solutions and concentrations:

Bistris–acetate buffer	0.02 *M*, pH 7.2, 25°C
Acetonitrile	0.66% (v/v)
Salicylaldoxime	1×10^{-4} *M*
Nitrophenylcarboxylate	5×10^{-6} *M* or 1×10^{-5} *M*
Polymer	1×10^{-5} *M* to 1×10^{-2} *M* in lauryl or naphthyl side chains

Bistris [N,N-bis(2-hydroxyethyl)imino-tris(hydroxymethyl)methane, $\mathrm{p}K_a = 6.5$] was chosen for suitable buffering capacity and relatively low ionic strength at pH 7.2. In addition, the ionizing group of Bistris is a sterically hindered tertiary amine, unlikely to react to any significant extent with nitrophenylcarboxylates. Acetic acid was used to adjust the pH of the buffer because acetate ion is a more compatible counter ion for polymer solubility than is chloride ion. Acetonitrile was the solvent for stock solutions of salicylaldoxime and nitrophenyl esters. The volume percentage of acetonitrile in reaction mixtures was kept to a minimum because rates of oxime acylation in the presence of quaternized polyethylenimine derivatives were found to decrease as the concentration of acetonitrile increased.

Good pseudo-first-order kinetics for oxime acylation were observed at all concentrations of polymer under conditions of excess salicylaldoxime over nitrophenylcarboxylate (10- to 20-fold excess). All values of k_{obs} were corrected for background rates (generally less than 1% of k_{obs}) of nitrophenyl ester hydrolysis in the absence of salicylaldoxime but in the presence of polymer. In general, values of k_{obs}, the pseudo-first-order rate constant for acylation of salicylaldoxime with nitrophenyl ester, increased to a maximum and then slowly decreased as the concentration of quaternized polyethylenimine increased. Therefore, concentration ranges of polymer were chosen to be at least wide enough for k_{obs} to have reached a maximum value.

Pseudo-first-order rate constants, k_{obs}, for the acylation of salicylaldoxime with *p*-nitrophenylcaproate were determined in the presence of varying concentrations of 10, 25, and 50% lauryl quaternary polyethylenimine acetate. Plots of k_{obs} versus

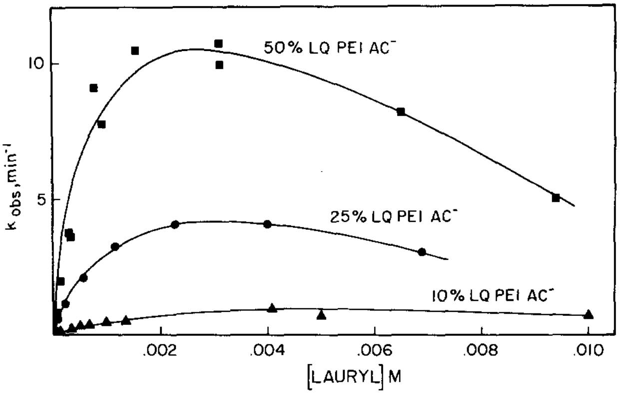


FIG. 1. Pseudo-first-order rate constants for the acylation of salicylaldoxime with p-nitrophenylcaproate in the presence of lauryl quaternary PEI derivatives. Reaction conditions: Bistris–acetate, 0.02 M, pH 7.2, 25°C; acetonitrile, 0.68% (v/v); salicylaldoxime, 1.0×10^{-4} M; and p-nitrophenylcaproate, 4.8×10^{-6} M. (▲) 10% lauryl quaternary PEI acetate, (●) 25% lauryl quaternary PEI acetate, (■) 50% lauryl quaternary PEI acetate.

concentration of polymer lauryl groups are shown in Fig. 1. Values of k_{obs} rose to a maximum and then slowly decreased as the concentration of polymer increased. Maximum values of k_{obs} increased as the degree of laurylation of the quaternary polyethylenimine derivative increased from 10 to 50%. Similar trends were observed with naphthyl quaternized polymers but their catalytic effectiveness is substantially less than that of the lauryl derivatives (*5*).

In this transacylation reaction, as in the decarboxylation one described previously (*18*), added chloride ions produce a marked attenuation in rate. As little as 0.007 M KCl reduced k_{obs} by half (Fig. 2). There may be ionic strength effects reducing the attractive interactions between cationic polymer and anionic substrates. Also ionic strength increases may contribute to micellar aggregation of substrate. Most important, probably, is a direct competitive binding of Cl^- ion to the cationic polymer with parallel displacement of anionic substrates.

With an anionic nitrophenylcarboxylate, 3-nitro-4-acetoxybenzoic acid, values

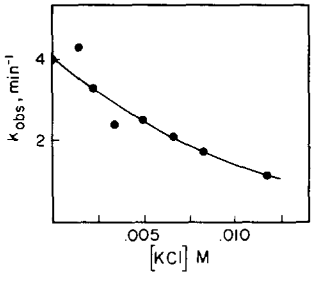


FIG. 2. Influence of potassium chloride concentrations on the pseudo-first-order rate constants for acylation of salicylaldoxime with p-nitrophenyllaurate in the presence of 25% lauryl quaternary PEI acetate. Reaction conditions: Bistris–acetate, 0.02 M, pH 7.2, 25°C; acetonitrile, 0.66% (v/v); salicylaldoxime, 1.0×10^{-4} M; p-nitrophenyllaurate, 4.8×10^{-6} M; and 25% lauryl quaternary PEI acetate, 1.0×10^{-3} M lauryl.

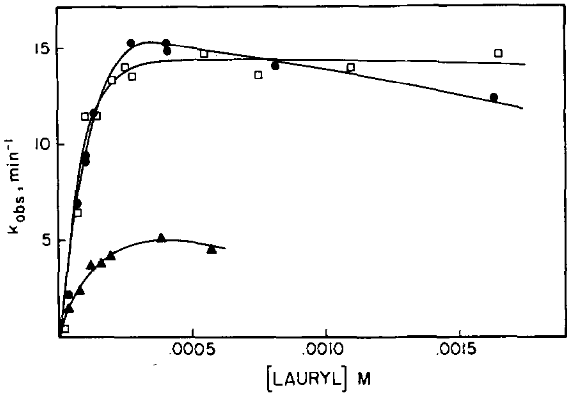


FIG. 3. Pseudo-first-order rate constants for acylation of salicylaldoxime with 3-nitro-4-acetoxybenzoic acid in the presence of lauryl quaternary PEI derivatives. Reaction conditions: Bistris–acetate, 0.02 M, pH 7.2, 25°C; acetonitrile, 0.66% (v/v); salicylaldoxime, 1.0×10^{-4} M; and 3-nitro-4-acetoxybenzoic acid, 1.0×10^{-5} M. (▲) 10% lauryl quaternary PEI acetate, (●) 25% lauryl quaternary PEI acetate, (☐) 50% lauryl quaternary PEI acetate.

of k_{obs} for acylations of salicylaldoxime in the presence of quaternized polymers were considerably higher than those for the uncharged nitrophenylcaproate (Fig. 3). Moreover, the maximum value of k_{obs} obtained in the presence of 50% lauryl quaternized polyethylenimine was essentially the same as that with the 25% lauryl polymer (Fig. 3) in marked contrast to the behavior with uncharged substrate (Fig. 1). Also, with the anionic substrate, maximum accelerations in rates were observed at much lower polymer concentrations.

A comparison of pseudo-first-order rate constants for acylation of salicylaldoxime with p-nitrophenylcaproate in the presence of 50% lauryl quaternized polyethylenimine and micelle-forming dodecyltrimethylammonium chloride is presented in Fig. 4. The contrast is striking, both in height of the maximal rate achieved and in the molar concentration of lauryl groups at which the maximum rate is attained. With polymer, the maximal k_{obs} is 17 times greater than with C_{12}-micelle, and the maximum is achieved at about 20 times lower concentration of lauryl groups. Perhaps even more important is the behavior at very low concentrations of catalyst. The polymer effects accelerations in rate as soon as any is added to the solution. The detergent is totally ineffectual until the critical micelle concentration is reached; afterward the rates rise slowly. The rate that is maximal for the micelle and is reached near 0.025 M lauryl groups, is achieved by 0.0001 M lauryl groups in the quaternized polymer.

Even if one compares the C_{12}-polymer with a C_{16}-detergent, the former excels (Fig. 4). Thus maximum catalytic activity was observed with 50% lauryl quaternized polyethylenimine at a C_{12}-group molar concentration five times lower than the molar concentration of C_{16}-group provided by micellar hexadecyltrimethylammonium chloride; and the maximal k_{obs} for the former was almost three times greater. Clearly the polymer is much superior to the micelle as a catalyst in this reaction. In effect the energy and negative entropy needed to form clusters on the polymer matrix have been supplied during the synthesis of the macromolecule.

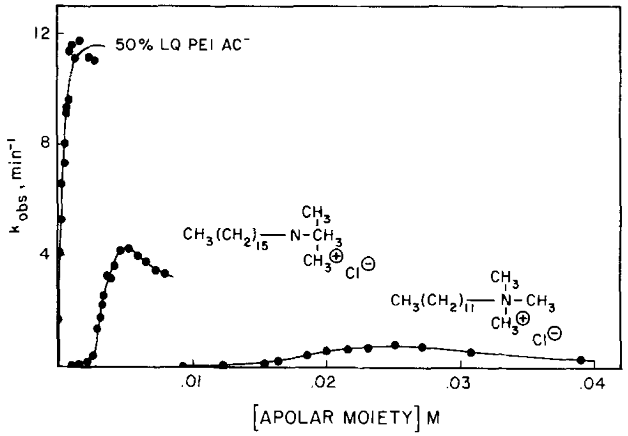
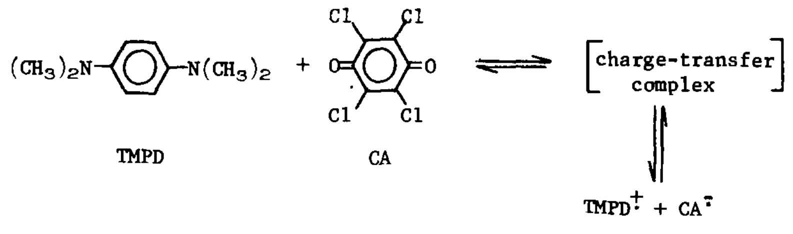


FIG. 4. Comparison of pseudo-first-order rate constants for acylation of salicylaldoxime with *p*-nitrophenylcaproate in the presence of 50% lauryl quaternary PEI acetate and two micelle-forming quaternary ammonium salts, hexadecyltrimethylammonium chloride and dodecyltrimethylammonium chloride. Reaction conditions: bistris–acetate, 0.02 *M*, pH 7.2, 25°C; acetonitrile, 0.66% (v/v); salicylaldoxime, 1.0 × 10^{-4} *M*; and *p*-nitrophenylcaproate, 4.8 × 10^{-6} *M*.

Behavior of Radical Ions

In view of the role the environment plays in donor–acceptor electron transfer in photosynthesis (*19*), it has seemed of interest to examine the effect of polyethylenimines on such transfer processes in model systems. For this purpose, we have focussed attention primarily on the pair tetramethyl-*p*-phenylenediamine (TMPD) and chloranil (CA), electron donor and acceptor, respectively. A charge transfer complex that may be formed should dissociate readily in a polar solvent (*20*) into a radical cation and anion:



[5]

Figure 5 illustrates the time dependence of the spectrum of an aqueous solution of TMPD and CA, in an 0.05 *M* tris(hydroxymethyl)aminomethane (Tris) buffer at pH 7.4. The twin peaks at 422 and 454 nm have been assigned (*21, 22*) to chloranil anion radical CA^{-}, and the other pair of peaks at 555 and 605 nm belong to the tetramethylphenylenediamine cation radical $TMPD^{+}$. As the spectra reveal (Fig. 5), in aqueous buffer both radical ions decreases in concentration with time. In marked contrast, however, is the behavior in the presence of a laurylated quaternized polyethylenimine (IV) [stoichiometric composition, $(C_2H_4N)_m(C_{12}H_{25})_{0.25m}(CH_3)_{1.6m}$]. At polymer concentrations near 10^{-4} residue-molar, the

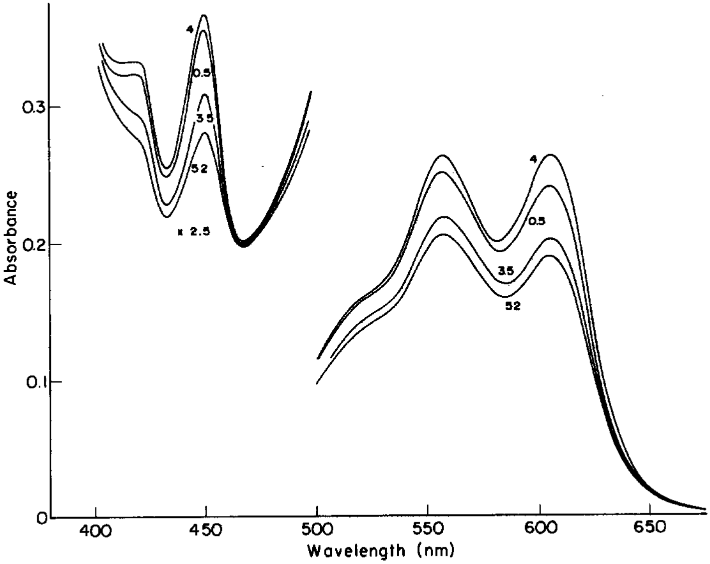


FIG. 5. Time dependence of spectrum of an aqueous solution of TMPD and CA in an 0.05 *M* Tris buffer, pH 7.4. $(CA)_0 = (TMPD)_0 = 2.5 \times 10^{-5}$ *M*. Time in minutes after mixing shown adjacent to each curve.

concentration of cation radical $TMPD^+$ increases with time whereas that of the anion radical $CA^{\bar{\cdot}}$ drops rapidly (Fig. 6). Particularly to be noted is the isosbestic point for the $CA^{\bar{\cdot}}$ spectra which implies a relationship between the

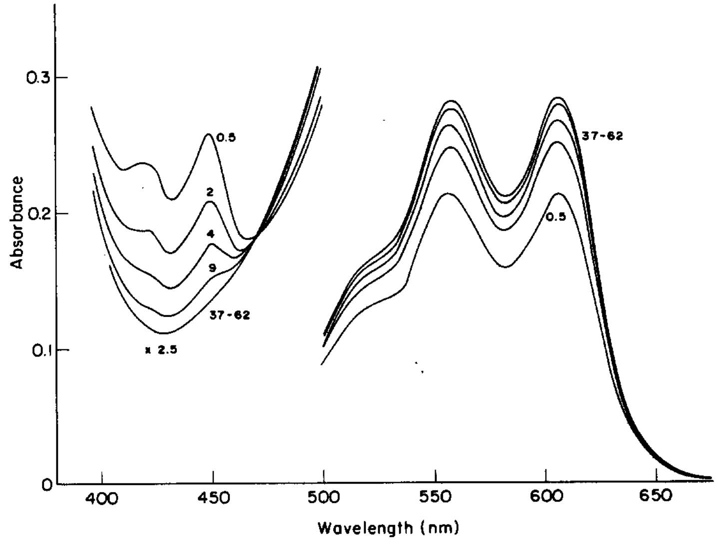


FIG. 6. Time dependence of spectrum of an aqueous solution of TMPD and CA in the presence of 3×10^{-4} residue-molar laurylated, quaternized polyethylenimine, (IV), in an 0.05 *M* Tris buffer, pH 7.4. $(CA)_0 = (TMPD)_0 = 2.5 \times 10^{-5}$ *M*.

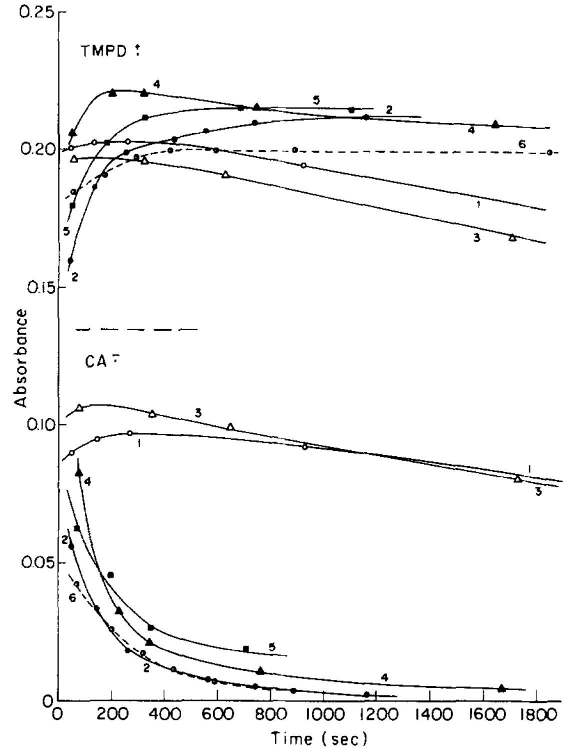


FIG. 7. Variation with time of relative concentrations of TMPD^{+} cation radical and of CA^{-} anion radical in presence of different additives: 1, none; 2, laurylated quaternized polyethylenimine, (IV), 3.0 × 10^{-4} residue-molar; 3, quaternized polyethylenimine, (V), 5.0 × 10^{-4} *M*; 4, cetyltrimethylammonium bromide, 3.4 × 10^{-4} *M*; 5, lauryltrimethylammonium chloride, 3.3 × 10^{-3} *M*; 6, laurylated quaternized polyethylenimine, 3.0 × 10^{-4} *M*, purged of oxygen before mixing. $(\mathrm{CA})_0 = (\mathrm{TMPD})_0 = 2.5 \times 10^{-5}$ *M*.

decay of CA^{-} and the rise of TMPD^{+}. It should be recognized, however, that cationic TMPD^{+} is likely to be expelled from the (cationic) environment of the quaternized polyethylenimine, whereas the CA molecules may reside in or near the surface of the polymer.

A quaternized polyethylenimine without lauryl groups (V) [stoichiometric composition, $(\mathrm{C_2H_4N})_m(\mathrm{CH_3})_{1.6m}$], however, does not accelerate the disappearance of CA^{-} radical (Fig. 7). Evidently electrostatic interaction alone is inadequate to bind the radical ions.

The kinetics of optical changes were examined also in a series of solutions of fixed chloranil, CA, concentration but increasing tetramethylphenylenediamine, TMPD, concentrations. Little change in rate of disappearance of CA^{-} was observed. In the complementary experiment, fixed TMPD, increasing CA concentrations, only minor changes in TMPD^{+} appeared. Evidently the dissociation equilibrium of the donor–acceptor pair, possibly through an intermediate charge-transfer complex, favors strongly the individual radical ions.

The behavior of the tetramethylphenylenediamine–chloranil combination can be rationalized in terms of the following mechanistic scheme:

$$\text{TMPD} + \text{CA} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{TMPD}^{\dot{+}} + \text{CA}^{\dot{-}}, \qquad [6]$$

$$\text{CA}^{\dot{-}} + \text{CA}^{\dot{-}} \xrightarrow{k_2} \text{CA} + \text{CA}^{2-}, \qquad [7]$$

$$\text{TMPD}^{\dot{+}} + \text{CA} \xrightarrow{k_3} \text{X}. \qquad [8]$$

In the equilibrium of Eq. [6], a charge-transfer complex may be an intermediate. However, this complex is not shown explicitly because its characteristic absorption band, near 800 nm (*20*), could not be detected. Thus the complex, if formed in an aqueous medium, dissociates promptly and essentially completely into the radical ions. The second reaction, Eq. [7], is a disproportionation step in which an electron transfer occurs from one radical anion to another. It is not surprising that this transfer is facilitated in the cationic and hydrophobic environment of quaternized laurylated polyethylenimine. Since the quaternized polymer without hydrophobic groups is ineffective in accelerating this reaction, it is clear that apolar as well as electrostatic interactions are essential. This feature is similar to that described above in the transacylation of nitrophenylcarboxylates to aldoximes. On the other hand, there are many circumstances in which cationic polyelectrolytes accelerate reactions between two negatively charged species primarily by electrostatic, thermodynamic effects (*23*).

The cation radical $\text{TMPD}^{\dot{+}}$ decreased slowly in concentration in aqueous buffer alone. In the presence of quaternized laurylated polymer, no decrease of $\text{TMPD}^{\dot{+}}$ was observed unless the initial concentration of CA exceeded that of TMPD. Therefore, the drop in concentration of $\text{TMPD}^{\dot{+}}$ must reflect a reaction with one of the three species produced by chloranil, CA, $\text{CA}^{\dot{-}}$, or CA^{2-} (Eq. [8]). The most likely candidate is CA. If $\text{CA}^{\dot{-}}$ were the reactant, the two ionic radicals $\text{TMPD}^{\dot{+}}$ and $\text{CA}^{\dot{-}}$ should decline at similar rates in the absence of polymer, where the disproportionation reaction, Eq. [7], is virtually nonexistent. The actual rates of decline (Fig. 7) do not fit this expectation. It is also unlikely that CA^{2-} (or CAH^- at pH 7.4) is the reactive species in Eq. [8] since the decrease in concentration of $\text{TMPD}^{\dot{+}}$ is sharper when the disproportionation reaction producing CA^{2-}, Eq. [8], is sluggish.

Equations [6]–[8] can also account for the presence of the isosbestic point observed in the presence of quaternized laurylated polyethylenimine. When two $\text{CA}^{\dot{-}}$ radicals disproportionate to yield one CA and one CA^{2-}, the former can react with TMPD to produce one $\text{TMPD}^{\dot{+}}$ and one $\text{CA}^{\dot{-}}$ (Eq. [6]). Thus the net result is a decrease of one $\text{CA}^{\dot{-}}$ molecule and an increase of one $\text{TMPD}^{\dot{+}}$.

The kinetics of the reactions of Eqs. [6]–[8] can also be analzyed quantita- The differential equations for the time dependence of concentrations of CA, TMPD, $\text{TMPD}^{\dot{+}}$ and $\text{CA}^{\dot{-}}$ cannot be solved in close form, but if we make a steady-state approximation, i.e., assume $d(\text{CA})/dt = 0$, we can obtain the following linear form

$$\frac{1}{(\text{CA}^{\dot{-}})_t} = \frac{1}{(\text{CA}^{\dot{-}})_{t=0}} + k_2 t, \qquad [9]$$

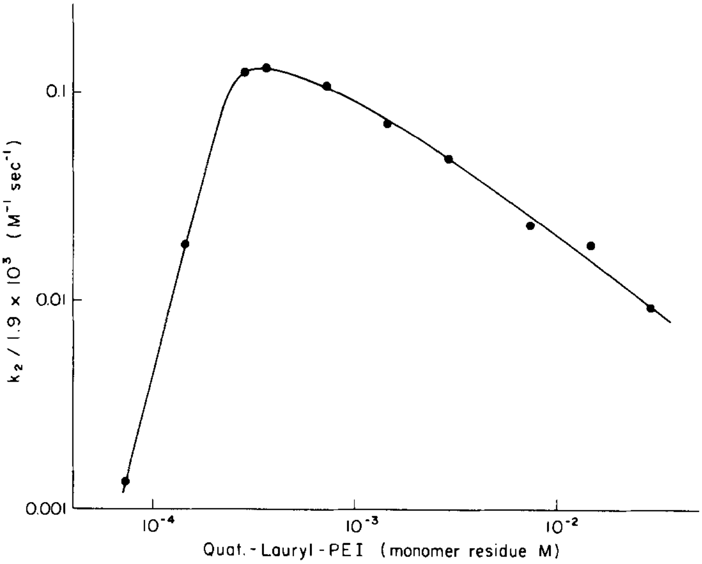


FIG. 8. Rate of disproportionation of chloranil anion radicals as a function of concentration of polymer, laurylated quaternized polyethylenimine, (IV). $(CA)_0 = (TMPD)_0 = 0.625 \times 10^{-4}$ *M*.

where *t* represents the time. Experimental data fitted to Eq. [9] led to values of k_2 for different concentrations of polymer (Fig. 8). As in the transacylation described above, this second-order rate constant increases with polymer concentration, reaches a maximum and then decreases. At the maximum, k_2 is more than 100-fold greater than the rate in the absence of polymer. At higher polymer concentrations, the rate drops because of the increasing likelihood that CA^- radicals will reside in separate macromolecular matrices.

Comparisons were also made of the relative effectiveness of cationic micelles as compared to cationic apolar polyethylenimines. Lauryltrimethylammonium chloride, $C_{12}H_{25}N(CH_3)_3^+ \cdot Cl^-$, at a concentration of 3.3×10^{-4} *M* had no effect on the kinetic pattern of the radical ions. At this concentration of lauryl groups, quaternized laurylated polyethylenimine produced a pronounced acceleration in rate of disappearance of anionic radicals (Fig. 7). At a concentration of 3×10^{-3} *M*, lauryltrimethylammonium micelles did show a kinetic acceleration. With a longer chain detergent, cetyltrimethylammonium bromide, $C_{16}H_{33}N(CH_3)_3^+ \cdot Br^-$, the kinetic acceleration at 3.4×10^{-4} *M* concentration was comparable to that of the lauryl polymer. It is of interest that such an effect was observed below the critical micelle concentration, 9×10^{-4} *M* (*24*). Similar behavior at premicellar concentrations has been described in some photochemical processes (*25, 26*). With both C_{12}- and C_{16}-detergents, a maximum in rate acceleration and a subsequent drop was observed at high concentrations. As in the polymer, at high concentrations of micellar species the reactive anion radicals are kept apart in different matrices.

CONCLUSION

In general, the apolar polymers are much more effective catalysts than are the corresponding detergent micelles. The high local densities of apolar groups on the polymer framework lead to cluster formation, which prevails even at the lowest polymer concentrations. Furthermore, the covalent attachment of the apolar groups to the polymer framework counterbalances any entropic tendencies of the constituents of the cluster to diffuse apart into the bulk solvent. Thus hydrophobic quaternized polyethylenimines provide environments that facilitate chemical changes that otherwise would not occur readily in aqueous solution.

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