A Study on the Mechanism of the Reaction of *N*-(2,4-Dinitrophenyl)-3-carbamoylpyridinium Chloride with Amines and Amino Acids with Reference to Effect of Polyelectrolyte Addition

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Abstract: The reaction of *N*-(2,4-dinitrophenyl)-3-carbamoylpyridinium chloride (I) with amines and/or OH^- was studied in aqueous media at 25 °C, using the rapid-scanning stopped-flow method. Two intermediates were observed at 460 and 380 nm. The appearance of the intermediate at 460 nm showed a first order dependence on $[OH^-]$, irrespective of the amines and their concentrations, and the second-order rate constant was $6 \times 10^4\ M^{-1}\ s^{-1}$. The absorption at 370 nm, which was strongly dependent on the amines, increased with time and passed through a maximum. The absorption at 350 nm, due to a by-product, 2,4-dinitroaniline, stayed practically constant with time at first and then increased. Addition of polymeric, surfactant, and simple electrolytes decreased the rate of the appearance of the 460-nm intermediate, indicating that the process was between oppositely charged ionic species. Hydrophobic polymeric anions accelerated the disappearance of the 370-nm intermediate, which indicated that the intermediate reacted with positively charged amines. On the basis of these data, a reaction mechanism was proposed.

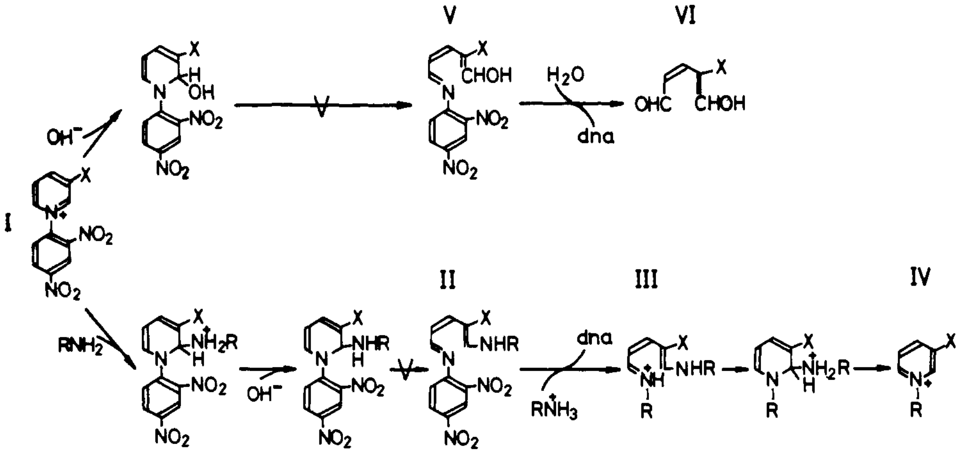
Pyridine and its derivatives are known to be quaternized with 2,4-dinitrophenyl chloride to produce quaternary salts, such as *N*-(2,4-dinitrophenyl)pyridinium chloride, which easily react with amines and other bases. This reaction was studied at the beginning of this century by Zincke et al.,[1] and later it was applied to the quantitative analysis of nicotinamide derivatives in biological systems[2] and to the synthesis of cyanine dyes.[3] Recently it was employed in the syntheses of novel coenzyme model compounds[4,5] and catalytic polyelectrolytes.[6]

According to kinetic studies so far made on the reaction of I with aniline derivatives,[7-11] the reaction is believed to proceed via cleavage of pyridine ring as is shown in the scheme and the intermediates, II and III, have large absorption maxima in the range of 450-500 nm (deep red) because of their conjugated structures. By ring closure, the intermediate III turns to the final product of a pyridinium salt with a new substituent at N_1 (IV), which has no absorption in the visible region. This step of the reaction (III → IV) was reported to be facilitated by addition of either acid or base, though kinetic profile of acid addition was found to be more complicated.[9] At the same time I can react with hydroxide ions to give another deep red substance (V), and therefore in the alkaline region both reactions (with amine and with OH^-) occur concurrently. The rate-determining steps of the intermediate (II and III) formation process were considered to be those of ring cleavage.

In view of the versatile applicability of this reaction, the reaction mechanism with other amines than aniline derivatives and also with amino acids are investigated in the present paper. In the authors' laboratory ionic reactions have been shown to be affected by addition of polyelectrolytes.[12] The mode of the influence certainly depends on reactants (or interactions) present. Conversely, it would be possible to infer, at least, the nature of the reactant by observing the electrolyte influence. (Actually, this type of reasoning was employed to demonstrate the separate existence of the hydrated electron.[13]) Thus we intend to obtain detailed information on the mechanism of this reaction by examining the influence of polyelectrolyte addition.

Experimental Section

Materials. *N*-(2,4-Dinitrophenyl)-3-carbamoylpyridinium chloride, which corresponded to I in the scheme, was prepared according to the method described by Lettré et al.[5] Amines and amino acids were of commercially available highest grade reagents



dna : 2,4-dinitroaniline
X : carbamoyl group

[Fluka AG (Buches, Switzerland), Sigma Chemical Co. (St. Louis, Calif.), or Wako Pure Chemicals (Tokyo, Japan)] and were used without further purifications. Buffers (carbonate, borate, and phosphate) were prepared from the commercially available guaranteed reagents. Deionized water was distilled by using an auto still (Yamato WAG-24) for preparation of aqueous solutions. Sodium poly(styrenesulfonate) (NaPSt) was purchased from Polyscience (Warrington, Pa.) (Lot No. 20-11, molecular weight 100 000). Sodium poly(ethylenesulfonate) (NaPES), degree of polymerization 770, was kindly donated by the Hercules Powder Co. (Wilmington, Del.). Dilute solutions of these anionic polyelectrolytes were converted to the acid form by passing them through columns of cation- and anion-exchanger resins. The conversion was checked by a flame test and finally they were neutralized with sodium hydroxide. The copolymer of diethyldiallylammonium chloride and sulfur dioxide (DECS) is a strong basic polyelectrolyte prepared by Harada et al.[14] The detail about poly(4-vinyl-*N*-*n*-propylpyridinium bromide) (C_3PVP) was described in a previous paper.[15] Sodium lauryl sulfate (NaLS) and cetyltrimethylammonium bromide (CTABr) were commercially available.

Kinetic Measurements. Three kinds of spectrophotometers were used for kinetic measurements. For identification of the absorption band of the intermediates and for preliminary kinetic measurements, a rapid-scanning stopped-flow spectrophotometer (Hitachi RSP-2) was applied. The details of this apparatus were described before.[16] The time necessary for a scan from 200 nm to 700 nm was 150 ms and three scans in 1 s after the mixing of the reactant solutions could be made. The rapid appearance of the absorption of the intermediate around 470 nm was followed at a fixed wavelength with a stopped-flow spectrophotometer (Union, RA1100) with a dead time less than 1 ms. Detailed description of this apparatus was given in a previous work.[17] For slower processes of the disappearance of the intermediate absorption and of the appearance of the final by-product, a high sensitivity spectrophotometer (Union SM-401) was used. This spectrophotometer uses a double-beam system with a head-on type single photomultiplier and affords a high sensitivity of 0.01 optical density in the full scale. In this case a syringe was applied to inject reactant solutions into the optical cell and the process from 5 s after the injection was followed. In all these spectrophotometers, thermostated water (in most cases at 25 °C) was circulated through the jackets holding the observation cells to maintain the temperature of the reactant solutions constant. The pH of the solution was checked by a pH meter (Hiranuma RAT 101) immediately after the kinetic measurements.

In the studies so far made on this reaction,[7-11] kinetic measurements had been carried out in ethanol–H_2O mixtures with various ethanol contents. In the present study, however, we used mainly aqueous solutions for the following two reasons. First, preliminary studies in the mixed solvents had shown that the appearance of the intermedial red substance did not obey a simple exponential function, but showed a very rapid uprise followed by a much slower increase, whereas the appearance in aqueous solutions was exponential. The second reason is the possibility of precipitation of polyelectrolytes in the mixed solvents and the poor solubility of amino acids toward alcohol. In all measurements the pseudo-first-order condition was maintained by using a large excess of amines (50–100-fold over I). The concentration of I was kept at low levels to prevent precipitation of dinitroaniline from the reaction mixtures.

Results

A. The Intermediate Formation (τ_f Process). First we confine ourselves to the kinetics of the intermediate formation. The rapid-scanning trace observed for the I-β-phenethylamine in the visible region is shown in Figure 1. Evidently new absorption was observed at 460 nm. Since this absorption at first became larger with time and then became smaller, it could be ascribed to the intermediates (II, III, V, or VI), though it was not clear at this stage which of the intermediates was responsible for the absorption. Similar rapid-scanning traces were further obtained for various amines and OH^-, from which the relaxation time (τ_f) for the intermediate formation was calculated and shown in Figure 2 as a function of pH. Obviously, log τ_f is linear with respect to pH, but is essentially independent of the species of amines and their concentrations (between 10^{-3} and 5×10^{-3} M). Thus, the intermediate formation is determined by $[H^+]$ or $[OH^-]$ both for reactions with amine and with OH^-.

The next question, whether the ring cleavage really occurred as suggested in the scheme, was answered by proton NMR measurements. For the reaction of I with either OH^- or ethylamine, we could observe an upward shift of a set of the signals of pyridine ring from −8.0 to −9.5 ppm from

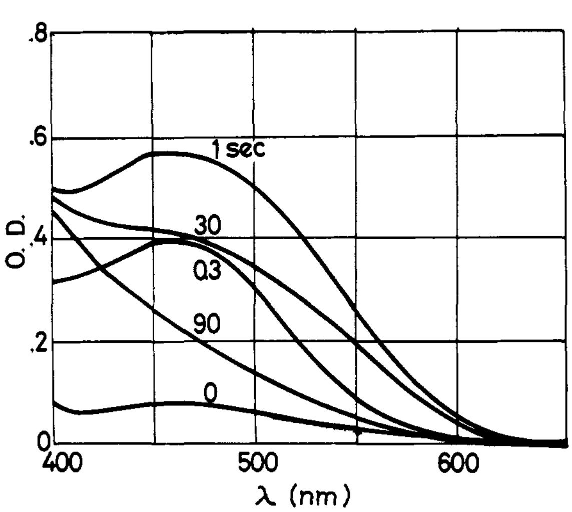


Figure 1. A typical oscilloscope trace by a rapid-scanning stopped-flow spectrophotometer in the visible region for the reaction of I with β-phenethylamine. The figures by the curve show the time (s) after the mixing of the reacting solutions. [amine] ≈ 2.5×10^{-3} M, [I] = 5×10^{-5} M, 0.05 M $NaHCO_3$–Na_2CO_3, pH 9.50.

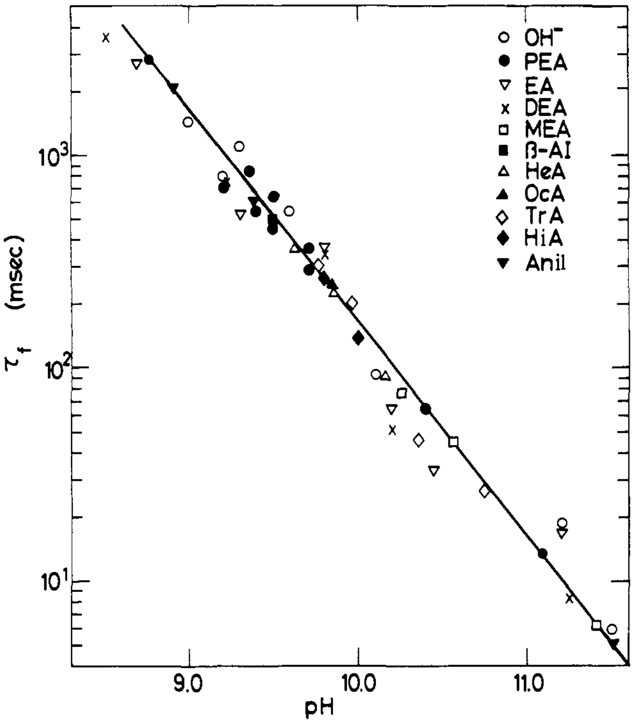


Figure 2. pH dependence of τ_f of reactions of I with various amines and OH^-, at different amine concentrations. [I] = 1×10^{-5} M, [amine] = $1\text{-}5 \times 10^{-3}$ M, 25 °C. ●, β-phenethylamine; ▽, ethylamine, ×, diethylamine; □, monoethanolamine; ■, β-alanine; △, hexylamine; ▲, octylamine; ◇, tryptamine; ◆, histamine; ▼, aniline; ○, NaOH. For octylamine, histamine, hexylamine, and tryptamine, 2.5% EtOH–H_2O media was used; 0.05 M phosphate, carbonate and borate were used as buffers.

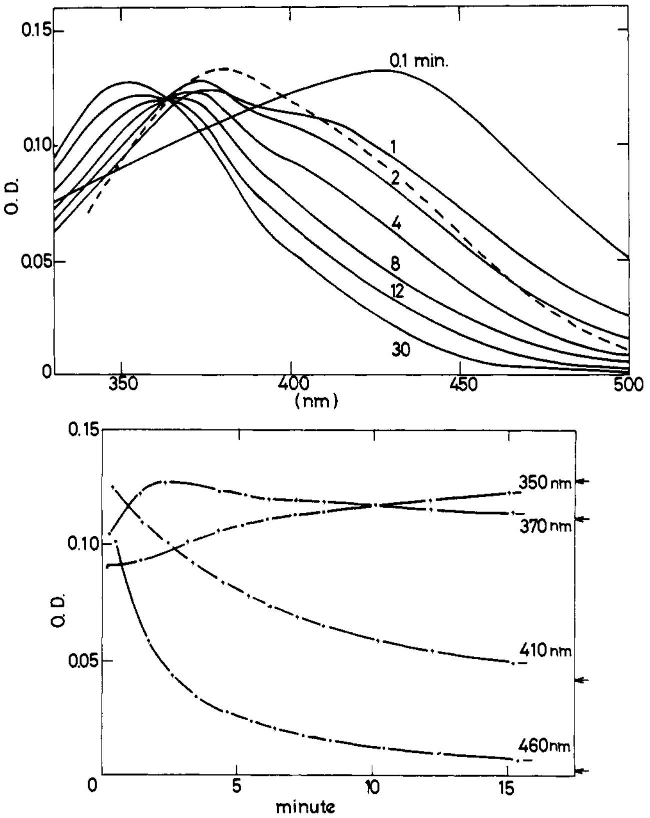


Figure 3. Changes of the absorption spectra during the intermediate-disappearing process of the reaction of I with β-phenethylamine. [I] = 5×10^{-5} M, [amine] = 2.5×10^{-3} M, 25°, 0.05 M $NaHCO_3$-Na_2CO_3, pH 9.35. (top), changes in the whole spectra. The figures by the curves show the time (min) when the scan was started from 330 nm after the initiation of the reaction. The scanning speed was 5 nm/s. For dotted curve, see the text. (bottom), changes with time at selected wavelengths. Each figure by the curve indicates the selected wavelength and the arrow at the right end shows the optical density at infinity.

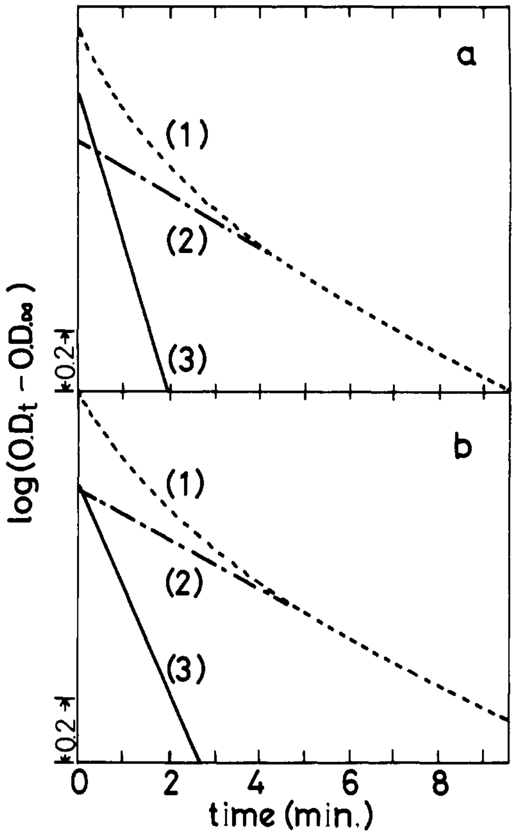


Figure 4. Two steps in the intermediate-disappearing process in the reaction of I with β-phenethylamine (a) and with hexylamine (b). [I] = 5×10^{-5} M, [amine] = 2.5×10^{-3} M. 0.05 M $NaHCO_3$-Na_2CO_3, pH 9.6, 25 °C. For b, 2.5% $EtOH$-H_2O mixture was used. Curve 1 (- - -), semilogarithmic plot of the observed values; curve 2 (- · · -), linear extrapolation of the latter part of curve 1; curve 3 (—), semilogarithmic plot of the difference between the curves 1 and 2.

Table I. Two Steps in the Intermediate-Disappearing Process Observed at 470 nm, 25 °C

Amine	pH[a]	$\tau_{s1}^{-1} \times 10^2$, s^{-1}	$\tau_{s2}^{-1} \times 10^3$, s^{-1}	pK_a[b]
Ethyl-	9.5	1.5	2.9	10.6
Hexyl-	9.5	1.4	3.2	10.6
Monoethanol-	9.4	1.2	2.8	9.5
β-Alanine	9.4	1.7	3.4	10.2
α-Alanine	9.4	1.4	3.0	9.7
Phenethyl-	9.4	1.8	3.3	9.8
Benzyl-	9.4	1.8	2.9	9.3
Trypt-	9.5	2.3	3.2	10.2
Aniline	9.4	1.4	3.4	4.6
OH^- (buffer only)	9.4	1.0	2.6	

[a] 0.05 M $NaHCO_3$-Na_2CO_3, 2.5% $EtOH$-H_2O, [amine] = 2.5×10^{-3} M. [b] From "Handbook of Biochemistry", 2d ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1973.

Me_4Si to −7.0 to −8.5 ppm by addition of the bases (Hitachi Perkin-Elmer 20-B).

B. Intermediate-Disappearing Process (τ_{s1} and τ_{s2} Processes). Figure 3a gives the spectral change (taken at intervals) of the reaction systems of I-β-phenethylamine in the course of intermediate-disappearing process. In Figure 3b, the spectral changes at fixed wavelengths are given as a function of time. In the presence of β-phenethylamine, the absorption at 460 nm decreased with time, and that at 370 nm showed a maximum whereas that at 350 nm due to dinitroaniline stayed practically constant at first and then increased monotonously. Figure 4 shows log (ΔOD) vs. time plots of the intermediate-disappearing process of the reaction of I with β-phenethylamine and also with hexylamine, measured at 460 nm. The whole trace can be clearly divided into two parts, the one proceeding with a time constant of several tens of seconds (τ_{s1}) and the other with that of several hundreds of seconds (τ_{s2}). Analysis showed that the rate (τ_{s1}^{-1}) of the rapid decrease at 460 nm was the same as that of the increase at 370 nm suggesting the direct change of the 460-nm intermediate into the 370-nm one. Furthermore, the rate (τ_{s2}^{-1}) of the slow decrease at 460 nm was equal to that of the decrease at 370 nm and at the same time to that of the increase at 350 nm. [Calculating with the kinetic constants given below and assuming that this spectral change is due to a sequential two-step mechanisms (see the Discussion) the new intermediate was shown to have a spectrum drawn by a dotted curve in Figure 3a and the true maximum absorption was found to be at 380 nm.] Intermediate-disappearing process was also observed for the reaction of I with OH^-, indicating that V and VI underwent further change into other species.

Table I contains the reciprocal of τ_{s1} and τ_{s2} in the intermediate-disappearing process of the reaction of several kinds of amines and amino acids and of OH^-. Generally, we note that the τ_{s1}^{-1} and τ_{s2}^{-1} values for the amine reaction are larger than those for the OH^- reaction and the value of τ_{s1}^{-1} at constant pH was found to be linear with respect to the amine concentration, as shown in Figure 5. Amines containing ring structures such as benzylamine, tryptamine, and β-phenethylamine had larger τ_{s1}^{-1}. Intro-

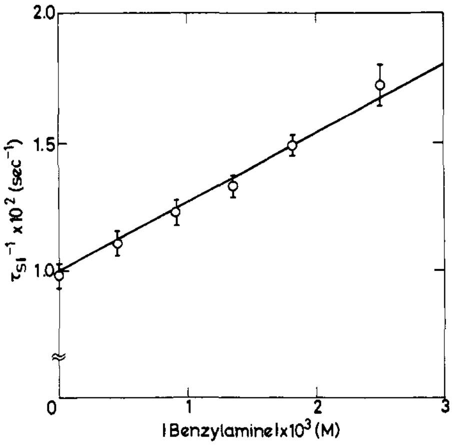


Figure 5. Amine concentration dependence of τ_{s1} for the reaction of I with benzylamine, 25 °C, [I] = 5 × 10^{-5} M, 0.1 M $NaHCO_3$-$NaCO_3$ buffer, pH 9.4.

duction of other functional groups, such as carboxyl (alanines) and hydroxyl (monoethanolamine) groups, into ethylamine had no great influences on the reactivity. As is shown in Table I, pK_a values of the amines were within the range of 9.3-10.6, except for aniline. No significant trend of the reactivity on pK_a of the amines was observed.

For ethylamine τ_{s1}^{-1} and τ_{s2}^{-1} were 1.5 × 10^{-2} and 2.9 × 10^{-3} s^{-1} at pH 9.5, 4.0 × 10^{-2} and 1.6 × 10^{-3} s^{-1}at pH 10.9, and 1.0 × 10^{-1} and 9.1 × 10^{-4} s^{-1} at pH 11.3 at [amine] = 2.5 × 10^{-3} M and at 25 °C. Evidently, as the pH increased, the τ_{s1}^{-1} became larger and the τ_{s2}^{-1} became smaller. This indicates that OH^- and H^+ are involved in the faster and slower steps, respectively.

C. Effect of Polyelectrolyte Addition on the τ_f Process. The effects of the addition of several kinds of electrolytes (polyelectrolytes, micelle electrolytes, and a simple electrolyte) were investigated in order to elucidate the nature of the intermediates. Observed effects on the τ_f process were shown by solid and broken curves in Figure 6. From the results so far obtained on the polyelectrolyte effects on various kinds of ionic reactions,[12] we know that addition of either cationic or anionic poly- and surfactant electrolytes causes deceleration for reaction between oppositely charged ionic species.[18] In the present system, polyelectrolyte addition always caused deceleration on the τ_f process as shown in Figure 6 [$(\tau_f)^{-1}/(\tau_f^0)^{-1} < 1$, the superscript 0 denotes the absence of electrolytes]. This indicates that the present reaction is occurring between a cationic species and an anionic species. Furthermore, the rather large deceleration by hydrophobic anionic electrolytes, NaPSt and NaLS, shows that the cationic reactant might be hydrophobic.

Table II. Effects of Polyelectrolyte Addition on the τ_{s2} Step of the Reaction with OH^- [a]

Added polyelectrolyte	Concn, equiv l.$^{-1}$	$(\tau_{s2})^{-1}/(\tau_{s2}^0)^{-1}$
NaPSt	2.5 × 10^{-3}	0.8
NaLS	5.0 × 10^{-3}	0.65
	2.0 × 10^{-2}	0.36
C_3PVP	1.0 × 10^{-2}	0.77
CTABr	5.0 × 10^{-4}	0.27

[a] 0.05 M $NaHCO_3$-Na_2CO_3 (pH 9.55), [amine] = 2.5 × 10^{-3} M.

D. Effect of Polyelectrolyte on the τ_s Process. First we note that the τ_{s1} process was hardly affected by the addition of polyelectrolytes, suggesting that the τ_{s1} process was between nonionic species.

As was mentioned, OH^- plays an important role in the τ_{s2} process in the presence of amines. Polyelectrolyte effects on this process of the OH^- reaction were studied first and the results are shown in Table II. In this case, deceleration was observed, suggesting that the process took place between oppositely charged ionic species.

Then, the polyelectrolyte influence on the reactions of β-phenethylamine and of ethylamine with I was studied, and the results are shown in Figure 7. From Table II and Figure 7, it is obvious that in the amine reaction, anionic electrolytes with hydrophobic residues such as NaLS and NaPSt caused acceleration, though they decelerated the OH^- reaction. The cationic micelle (CTABr) caused largest deceleration in both cases.

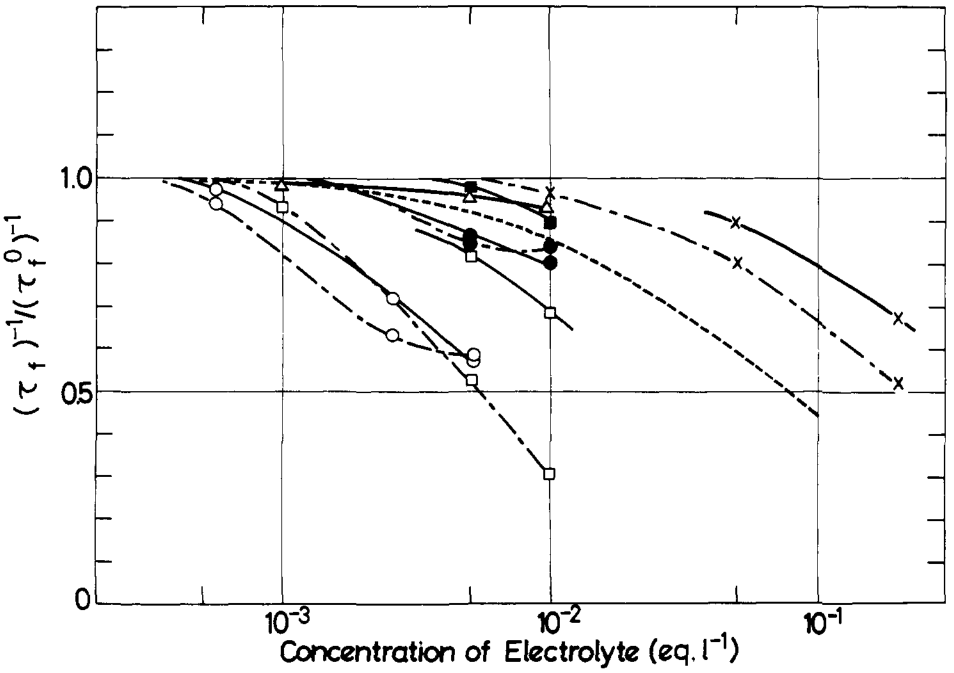


Figure 6. Effects of electrolytes on the τ_f process of the reactions with β-phenethylamine (solid lines) and with ethylamine (broken lines). [amine] = 3 × 10^{-3} M, pH 9.65, 0.05 M $NaHCO_3$-Na_2CO_3 buffer, [I] = 1 × 10^{-5} M; ○, NaPSt; □, NaLS; △, NaPES; ●, C_3PVP; ■, CTABr; ×, KNO_3; dotted line, calculated using Manning's theory.

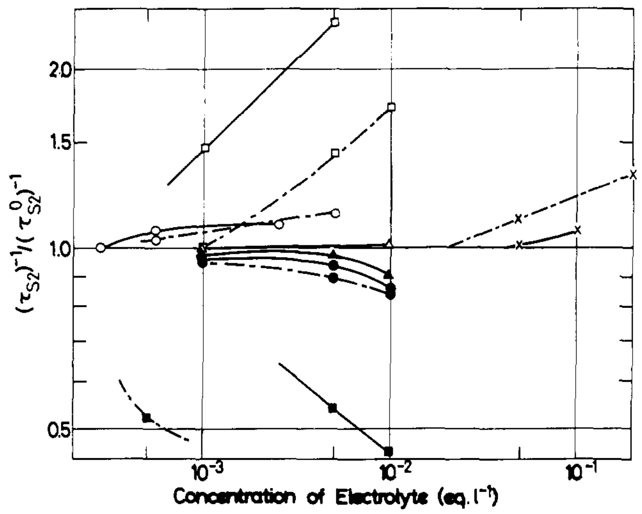


Figure 7. Effects of electrolytes on the τ_{s2} step of the reactions with β-phenethylamine (solid lines) and with ethylamine (broken lines). The conditions and symbols were the same as in Figure 6, except for ▲, DECS.

As is seen from Figure 7, $(\tau_{s2})^{-1}/(\tau_{s2}^0)^{-1}$ depended on amines used. Furthermore, when an amine with a rather large hydrophobic part, e.g., octylamine, was used, NaLS and NaPSt caused 6.9- and 5.7-fold accelerations at electrolyte concentrations of 1×10^{-2} and 5×10^{-3} equiv $l.^{-1}$, respectively, which was much larger than the results shown in Figure 7 for ethylamine (about 1.2-1.5). Though C_3PVP decelerated the process only by 7%, CTABr retarded it by 96% of that in the electrolyte-free system, at an electrolyte concentration of 1×10^{-2} equiv $l.^{-1}$ in 2.5% $EtOH-H_2O$.

Discussion

A. The τ_f Process. As was shown in Figure 2, the τ_f was essentially independent of the amine species and decreased linearly with increasing $[OH^-]$. This result can be interpreted as showing that the observed process was the rate-determining (nucleophilic) attack of OH^- to the (cationic) pyridinium ions (I). We recall here the deceleration of the τ_f process by polyelectrolytes shown in Figure 6 [Results (C)], which also indicated that the process took place between cationic and anionic species.

The second-order rate constant for the OH^- reactions calculated from Figure 2 was 6×10^4 M^{-1} s^{-1}.

Since this τ_f process was observed also for the amine reactions, the OH^- attack was inferred to be the first process of the entire reaction for both the OH^- reaction and amine reactions. Thus it is thought that the absorption at 460 nm is due to the intermediate V and that the possibility of the successive reactions (described in the scheme) of I with amine and subsequently with OH^- can be ruled out. Then a question arises how II is produced, which will be treated below.

It should be of interest to dissect here the observed polyelectrolyte influence on a theoretical basis. Using both Manning's theory on polyelectrolyte solutions[19] and the treatment reported in previous papers,[20,21] the $(\tau_f)^{-1}/(\tau_f^0)^{-1}$ values were estimated for reactions between univalent cations and univalent anions in the presence of either cationic or anionic polyelectrolytes. As the so-called charging parameter (ξ) of the Manning theory, we used a value of 2.85, which corresponded to the case of NaPES at 25 °C. The theory (dotted line in Figure 6) shows that polyelectrolytes should hinder the reaction, as was observed. The agreement between the theory and experiment, it should be noted, is better than originally expected for PES, but is unsatisfactory for PSt. This indicates the large contribution of the hydrophobic interaction (which was neglected in the Manning theory) between PSt anions and the reactants. Thus the present discussion definitely implies that, for the τ_f process, (negatively charged) OH^- reacts with (positively charged) hydrophobic pyridinium ions.

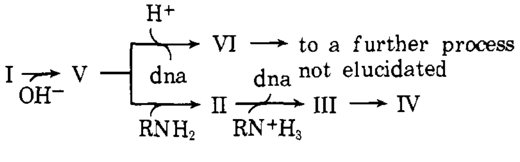
B. The τ_s Process. The τ_s process was divided into two processes of the relaxation times τ_{s1} and τ_{s2}. In the faster process, we believe that the intermediate V formed by the OH^- attack on I was directly converted into another intermediate whose absorption maximum was at 380 nm and this process was found to be a linear function of the amine concentration [Results (B)]. From the time change of the 370-nm absorption (Figure 3b), the latter intermediate is inferred to be consumed in the slower process to produce another intermediate and dinitroaniline. As a matter of fact, the 370-nm absorption decreased at the same rate as the increase in the 350-nm absorption (due to dinitroaniline). It is tempting to suggest that the intermediate at 380 nm is II (see the scheme) which is converted to the intermediate III and dinitroaniline.

Next we discuss the τ_{s2} process. As seen from Figure 7, anionic hydrophobic polyelectrolytes caused acceleration of the τ_{s2} process in the amine reactions whereas cationic hydrophobic polyelectrolytes showed deceleration, and polyelectrolytes (NaPES and DECS) which are not hydrophobic had very small influence. If the corresponding data obtained for octylamine [Results (D)] are compared with those for ethylamine (given in Figure 7), the hydrophobicity of the R group in amine (RNH_2) is seen to be an important factor determining the acceleration and deceleration. According to our previous finding of the cooperative action of electrostatic and hydrophobic interactions in polyelectrolyte catalysis,[12] these results indicate that the amine reaction under consideration contains hydrophobic neutral species reacting with cations. Remembering that τ_{s2}^{-1} was the rate of the decrease of absorption at 370 nm (due to II) and simultaneously the rate of the increase at 350 nm (dinitroaniline), we confirm that the hydrophobic neutral species is II and suggest that the cations are protonated amines (RN^+H_3). At pH employed (~9.6), the degree of protonation of the amines used is fairly high, except for aniline (see pK_a values in Table I). The contribution of protonated amine is furthermore consistent with the observation that the τ_{s2}^{-1} became smaller with increasing pH [Results (B)]. The τ_s process was also observed for the OH^- reaction. However, the spectral change at 370 nm was rather small so that quantitative argument was difficult.

The absorption of the intermediate III could not be observed in the visible region. It is inferred that the concentration of III must be small because it is quickly converted to the final product IV by very fast ring closure process.

Conclusion

All these consideration finally lead us to a conclusion that the observed τ_f corresponds to the process I → V *for both* the OH^- and the amine reactions and that the τ_s process of the amine reaction contains the steps from V to IV. It seems reasonable to consider that the τ_{s1} of the amine reaction corresponds to (V → II) and the τ_{s2} to (II → III), while (III → IV) is fast. The total course of the reaction can thus be written as follows.



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In Vitro Solar Conversion after the Primary Light Reaction in Photosynthesis. Reversible Photogalvanic Effects of Chlorophyll–Quinhydrone Half-Cell Reactions

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Abstract: In this publication, we report the observation of photogalvanic effects arising from chlorophyll a–quinhydrone (Q: H_2Q, 1:1) half-cell reactions. Platinum electrodes have been employed. In the presence of light, a photocurrent is developed as Chl a aggregates presumably undergo a charge-transfer interaction that results in the creation of a p-type semiconductor film. The observed photopotential at the Pt–Chl a electrode is positive. When the light is turned off, the half-cells regress toward the preillumination conditions, and a reverse current is observed. The spectral response of the photogalvanic effect has been determined. It has been found that a distribution of Chl a–H_2O aggregates contribute to the observed photocurrent. The in vitro solar conversion results are discussed in terms of the recently proposed primary light reaction model of photosynthesis.

Introduction

The primary processes of the reversible photochemical reaction involving benzoquinone (Q), hydroquinone (H_2Q), chlorophyll (Chl a), and the Chl a^+ cation in different solvent systems has been the subject of numerous investigations.[1-4] The overall reaction may be written

$$2\text{H}^+ + 2(\text{Chl a}) + \text{Q} \underset{\text{dark}}{\overset{h\nu}{\rightleftarrows}} 2(\text{Chl a}^+) + \text{H}_2\text{Q} \qquad (1)$$

in which Chl a and H_2Q act as the electron donor in the light and dark reactions, respectively. In this paper we describe our initial attempt at arriving at reversible photogalvanic action derived from photoelectrochemical interactions between Pt–Chl a and quinhydrone electrodes. The motivation of the present work differs from earlier observations of photoconductive and photoelectrochemical effects of chlorophyll[5-7] and other systems[8-11] in that we shall adopt the rigorous definition of a galvanic cell in which power is derived from spontaneous chemical reaction between two half-cells. The light perturbation should lead to photoelectrochemical effects that may be generically related to the Becquerel effect.[8,9] However, the present results may be of special interest because of the near-infrared photoactivity of Chl a. Most existing photoelectrochemical cells operate in the blue or near-ultraviolet.[10-13]

The proposed photogalvanic cell may be written

$$\text{Pt, }\underset{\text{A}}{\text{Chl a}|\text{Chl a}^+}|\text{LiClO}_4\|\text{NaOH, }\underset{\text{B}}{\text{NaHCO}_3|\text{H}_2\text{Q}}|\text{Q, Pt} \qquad (2)$$

Based on the reversible reactions given in (1), one might expect the Chl a-plated Pt electrode in (2) to develop a negative photopotential due to the photooxidation of Chl a by Q. In the following we report the observed behavior of the Chl a–quinhydrone photoelectrochemical cell. Contrary to our expectations, a positive photopotential has been observed at the Chl a-plated electrode, leading to the somewhat surprising conclusion that Chl a is in fact reduced by the quinhydrone cell under light conditions. It will be shown that this unexpected behavior can be readily accounted for in terms of the p-type semiconductor properties[6] of hydrated Chl a aggregates and of the characteristic photovoltaic behavior of binary compound semiconductors.[14]

Experimental Section

The Chl a was extracted from spinach and purified in the usual manner.[15] The purity of the sample was monitored by the peak positions and the peak ratio of the blue and red absorption bands of Chl a in diethyl ether,[15] cyclic voltametric measurements,[16] liquid