

2970, 2940, 1750, 1720, 1650, 1620, 1440, 1400, 1285, 1250, 1220, 1160 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) 1.86 (s), 1.87 (s) (6 H), 3.09 (s), 3.12 (s), 3.29 (m) (5 H), 3.90 (s, 3 H) ppm; UV (dioxane) 333 nm (ϵ 5500), 230 (13300); fluorescence (dioxane) 427 nm (ϕ_F 0.65); mass spectrum, m/e 262 (M^+).

9,10-Dioxa- μ -dicarboxymethylene-*syn*-(methylene,methyl)bimane (4e). Dimethyl ester **4b** (280 mg, 0.88 mmol) in trimethylsilyl iodide (800 mg, 4 mmol) was heated under N_2 at 100 $^\circ\text{C}$ for 15 h, the dark red mixture mixed with water (5 mL) and ether (15 mL), the suspension stirred for 15 min, and the solid filtered off and recrystallized to yield μ -((HOOC) $_2\text{C}$)-*syn*-(CH_2CH_3)**B** (**4e**): 175 mg (68%); bluish-white crystals (*i*-PrOH); mp 255 $^\circ\text{C}$; IR (KBr) 3480, 3200, 1715 (br), 1640, 1385, 1305, 1250, 1200, 1175, 1120, 1080, 790, 760 cm^{-1} ; $^1\text{H NMR}$ ($\text{Me}_2\text{SO}-d_6$) 1.70 (s, 6 H), 3.21 (s, 4 H) ppm; mass spectrum (CI), m/e 249 [($\text{M}+1$) $^+$ - CO_2].

9,10-Dioxa- μ -methylthiano-*syn*-(methylene,methyl)bimane Fluorosulfate (5a). μ -(*S*)-*syn*-(CH_2CH_3)**B** (**5**; 250 mg, 1.13 mmol) and methyl fluorosulfate (0.5 mL) were stirred together for 15 h, and CH_2Cl_2 (10 mL) and MeOH (10 mL) were then added. After the solid had dissolved, the solvent was removed and the residue recrystallized to yield μ -(CH_3S^+)-*syn*-(CH_2CH_3)**B** FSO_3^- (**5a**): 210 mg (56%); yellow powder (EtOAc + 5% CH_3CN); mp 210 $^\circ\text{C}$ dec; IR (KBr) 1760, 1680, 1630, 1385, 1180, 1160, 1070, 1020 cm^{-1} ; $^1\text{H NMR}$ ($\text{Me}_2\text{SO}-d_6$) 1.81 (s, 6 H), 2.89 (s, 3 H), 5.0 (m, 4 H) ppm; UV (CH_3CN) 356 nm (ϵ 6000), 256 (13700), 232 (21600); fluorescence (CH_3CN) 440 nm (ϕ_F 0.37).

9,10-Dioxa- μ -sulfono-*syn*-(methylene,methyl)bimane (5b). μ -(*S*)-*syn*-(CH_2CH_3)**B** (**5**; 224 mg, 1 mmol) and *m*-chloroperbenzoic acid (515 mg, 3 mmol) in CH_2Cl_2 (30 mL) were stirred for 3 h at 25 $^\circ\text{C}$, during which the initial suspension changed character. The solid was filtered off, washed, and recrystallized to yield μ -(SO_2)-*syn*-(CH_2CH_3)**B** (**5b**): 190 mg (75%); colorless crystals (CH_3CN); mp >300 $^\circ\text{C}$ (blackens >270 $^\circ\text{C}$); IR (KBr)

2980, 2920, 1775 (sh), 1760, 1700, 1660, 1645, 1410, 1370, 1345, 1270, 1195, 1170, 1150, 1090, 1075, 775, 760 cm^{-1} ; $^1\text{H NMR}$ ($\text{Me}_2\text{SO}-d_6$) 1.80 (s, 3 H), 4.95 (s, 2 H) ppm; UV (CH_3CN) 333 nm (ϵ 5750), 236 (17500); fluorescence (CH_3CN) 441 nm (ϕ_F 0.88); mass spectrum, m/e 254 (M^+).

Acknowledgment. We are grateful to Gilda Iny, Dov Faust, and Yonah (Cohen) Faust for various types of help during the course of the work, for partial support from a grant from the Israel Academy of Sciences, and to Professor R. Neidlein, Pharmazeutisch-Chemisches Institut, Universität Heidelberg, for help with the elemental analyses.

Registry No. 1, 68654-25-1; **2a**, 76421-31-3; **2b**, 76421-32-4; **2c**, 76421-33-5; **2d**, 76421-34-6; **2e**, 76421-35-7; **2f**, 76421-36-8; **2fa**, 76421-37-9; **2fa**₂, 76421-38-0; **2fa**₃, 76421-39-1; **2fa**₄, 76421-40-4; **2fl**, 76421-41-5; **2fl**₂, 76421-42-6; **2fl**₃, 76421-43-7; **2fp**, 76421-44-8; **2fp**₂, 76421-45-9; **2fp**₃, 76421-46-0; **2g**, 76421-47-1; **2h**, 76421-48-2; **2i**, 76421-49-3; **2j**, 76421-50-6; **2k**, 76421-51-7; **2l**, 76421-52-8; **2m**, 76421-53-9; **2n**, 76421-54-0; **2o**, 76421-55-1; **2p**, 76421-56-2; **2q**, 76421-57-3; **3a**, 76421-59-5; **3b**, 76421-60-8; **3c**, 76421-61-9; **4a**, 76421-62-0; **4b**, 76421-63-1; **4c**, 70090-46-9; **4d**, 76421-64-2; **4e**, 76421-65-3; **4f**, 76421-66-4; **5**, 74317-61-6; **5a**, 76421-68-6; **5b**, 74317-60-5; ammonium hydroxide, 1336-21-6; methylamine, 74-89-5; ethylamine, 75-04-7; *tert*-butylamine, 75-64-9; 2-aminoethanol, 141-43-5; tris(hydroxymethyl)aminomethane, 77-86-1; hydroxylamine hydrochloride, 5470-11-1; benzylamine, 100-46-9; 4-methoxybenzylamine, 2393-23-9; aniline, 62-53-3; 4-methylaniline, 106-49-0; 4-cyanoaniline, 873-74-5; 4-bromoaniline, 106-40-1; 4-chloroaniline, 106-47-8; 4-(carboxy)aniline, 94-09-7; 4-methoxyaniline, 104-94-9; diethyl malonate, 105-53-3; dimethyl malonate, 108-59-8; malononitrile, 109-77-3; acetic anhydride, 108-24-7; *N*-methyl-4-chloroaniline, 932-96-7; *N*,4-dimethylaniline, 623-08-5; palmitoyl chloride, 112-67-4; lauroyl chloride, 112-16-3; Na_2S , 1313-82-2.

Kinetics and Mechanism of the Reaction of 10-Phenylphenothiazine Dication with Water in Acetonitrile

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The reaction of electrogenerated 10-phenylphenothiazine (PPTZ) dication (PPTZ^{2+}) with water was investigated in acetonitrile containing 0.5 M NaClO_4 by cyclic voltammetry and controlled-potential electrolysis. The cyclic voltammogram of PPTZ showed two reversible redox waves at water concentrations of less than 3 mM at a scan rate of 0.2 V s^{-1} . When the water concentration was increased, the return peak for the second wave, which is due to reduction of the dication to the cation radical, disappeared, while the cation radical was still stable (up to at least 260 mM H_2O) during the time scale of the voltammetric measurements. By controlled-potential electrolysis (CPE) at 1.0 V vs. Ag/Ag^+ for 1–5 mM PPTZ solutions containing 20–260 mM water, anodically generated PPTZ^{2+} was found to react with water to give 5-hydroxy-10-phenylphenothiazinium ion ($\text{PPTZ}(\text{OH})^+$) which was further deprotonated by addition of an excess of water to the solution to form 10-phenylphenothiazine 5-oxide ($\text{PPTZ}(\text{O})$). The kinetic study using a cyclic voltammetric technique indicated that the rate law was given as $-\text{d}[\text{PPTZ}^{2+}]/\text{dt} = k_f[\text{PPTZ}^{2+}][\text{H}_2\text{O}]^2$ at various temperatures tested (–20 to +30 $^\circ\text{C}$), where $k_f = 2.4 \pm 0.5 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ at 25 $^\circ\text{C}$. From the kinetic data obtained, the activation enthalpy and activation entropy were estimated to be $\Delta H^\ddagger = 30.5 \text{ kJ/mol}$ (7.3 kcal/mol) and $\Delta S^\ddagger = -58.5 \text{ J/(mol K)}$ (–14 eu), respectively. The rate law and the activation parameters are explained in terms of the following reactions: $\text{PPTZ}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{PPTZ}(\text{OH}_2)^{2+}$, $\text{PPTZ}(\text{OH}_2)^{2+} + \text{H}_2\text{O} \rightarrow \text{PPTZ}(\text{OH})^+ + \text{H}_3\text{O}^+$ (rds), and $\text{PPTZ}(\text{OH})^+ + \text{H}_2\text{O} \rightleftharpoons \text{PPTZ}(\text{O}) + \text{H}_3\text{O}^+$, where the activation step is the nucleophilic attack by water to form a $\text{PPTZ}(\text{OH}_2)^{2+}$ - H_2O adduct following fast deprotonation to give $\text{PPTZ}(\text{OH})^+$. The stepwise process proposed for the nucleophilic attack by water on PPTZ^{2+} seems to be a rather usual reaction pathway in nucleophilic addition to dications.

The nucleophilic addition to anodically generated electrophiles such as cation radicals has been a subject of

much attention in recent electroorganic studies.¹ Reactions of cation radicals of 9,10-diphenylanthracene^{2–4} and

thianthrene⁵⁻⁷ with nucleophiles have been examined extensively. In particular, sulfur-containing heterocyclics have been interesting because of their anomalous behavior in the reaction; for example, pyridination of thianthrene cation radical gave a nucleophilic substitution product at a ring site, *N*-(2-thianthrenyl)pyridinium ion,⁸ while the other reagents gave nucleophilic addition products at sulfur atom.⁵ The precursors to the electrophiles usually show two consecutive one-electron oxidation processes (called an EE system),⁹ and cation radicals formed by the first one-electron oxidation are in equilibrium with dications, the two-electron oxidized product formed by disproportionation. Thus, in some cases, reactions of cation radicals with nucleophiles have been considered to be via dications⁵ because dications are far more reactive than cation radicals. Recently, however, Blount et al.^{1,3,4,7} have proposed that a half-regeneration mechanism (HRM) in which not dications but cation radicals react initially with nucleophiles is widely applicable rather than a disproportionation route. For further clarification of the extent to which the reaction of a dication contributes to the reaction of a cation radical with a nucleophile, a study of the reaction of a dication itself with a nucleophile would be useful. However, the kinetics and/or mechanism of the reactions of dications have not yet been examined in detail.

Thus, we have investigated the reaction of a dication with water as a nucleophile in acetonitrile by cyclic voltammetry. Thianthrene (TH) dication (TH²⁺) has been found to be highly reactive, and no return peak for the second wave of the EE process was observed even at the scan rate of 20 V s⁻¹ in an acetonitrile solution containing 1 mM TH and ca. 5 mM water; a reversible wave was reported only in a solution containing water scavengers¹⁰ or, recently, in liquid sulfur dioxide.¹¹ Thus, 10-phenylphenothiazine (PPTZ) was employed as a dication source because (i) introduction of a nitrogen atom can diminish the reactivity of the dication, like the case of the cation radical,¹² and (ii) *N*-substituted phenothiazine would be free from the complication resulting from the reaction at the nitrogen atom, unlike the case of phenothiazine.^{13,14} If the kinetics and mechanism of the reaction of the PPTZ²⁺ dication as a pilot reaction become clear, the reactivity of other dications whose reactions are similar to those of the pilot substance can be derived similarly by comparing, for example, peak current ratios in cyclic voltammograms of the substances of interest under given conditions.

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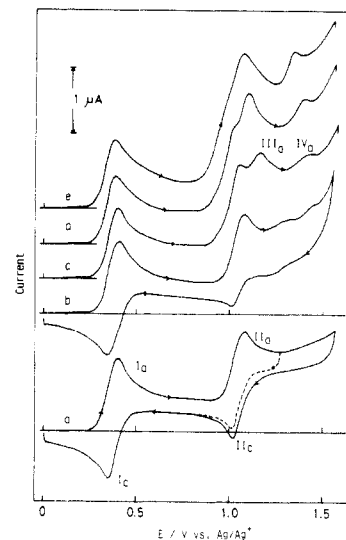


Figure 1. Cyclic voltammograms of 1 mM PPTZ at 25 °C in MeCN-0.5 M NaClO₄ containing various amounts of water: a, 3 mM; b, 14 mM; c, 30 mM; d, 80 mM; e, 650 mM. The scan rate was 0.2 V s⁻¹.

Phenothiazine and its derivatives have generated interest in their redox reactivity as physiologically important tranquilizers¹⁵ and recently as photoredox sensitizers for solar energy conversion cells.¹⁶ The study of the stability of dications, as well as that of cation radicals, can provide additional information for these applications.

Thus, in the present paper, the electrochemical behavior of PPTZ and the reaction of anodically generated PPTZ²⁺ with water are reported in detail.

Experimental Section

PPTZ was synthesized by a method similar to those described in the literature:^{12,17} colorless prism; mp 95.0-95.6 °C (lit.^{12,17} mp 94.5-95.5 °C); mass spectrum, *m/e* 275 (M⁺; calcd for PPTZ, *m/e* 275.4 (M)); UV_{max} (MeCN) 256 nm (log ε 4.67), 319 (3.56). Anal. Calcd for C₁₈H₁₃NS: C, 78.51; H, 4.76; N, 5.09. Found: C, 78.54; H, 4.82; N, 5.09. Acetonitrile and sodium perchlorate as the supporting electrolyte were purified by the usual method.¹⁸ The other reagents except where otherwise noted were GR grade and were used with no further purification. The residual water contained in acetonitrile was removed by using 4A molecular sieves (Wako) or Neosorb A (Shokubai Kasei) which were previously dried in an electric furnace at 400 °C for more than 6 h. The water contents in the test solutions were measured by using a Mitsubishi digital moisture meter, Model CA-02.

Cyclic voltammograms were obtained by using commercially available instruments¹⁸ at a platinum disk electrode (2 × 10⁻³ cm²). For the kinetic study the voltammograms were measured for 1 mM PPTZ solutions containing 2.6-150 mM water; at lower concentrations of water the dication was stable (the peak current ratios were more than 0.8) during the time scale of the voltammetric measurement even at the scan rate of 0.2 V s⁻¹, while at higher concentrations of water the second wave (II_a in Figure 1) due to dication formation merged into the third wave (III_a in

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Figure 1). The scan rates used were 0.2–80 V s⁻¹ to obtain the peak current ratios for the second wave ($i_{p_{II}}/i_{p_{II}}$) of 0.5–0.8, values which are suitable for accurate calculation for kinetics.¹⁹ The reversible redox potential, E_r , for the dication–cation couple was estimated¹⁹ from the cyclic voltammograms having completely reversible features (the peak current ratio, $i_{p_{II}}/i_{p_{II}}$, is unity, and the peak separation for the anodic and return peaks, $E_{pa} - E_{pc}$, is nearly equal to RT/F) at a given temperature: for example, 1.07 V at 25 °C. The switching potential, E_λ , at which the direction of the potential sweep was reversed was usually fixed at 1.3 V. The voltammograms in which the third wave does not appear up to 1.4 V were used for the kinetic study. The time in seconds, τ , required for the potential scan from E_r to E_λ was varied by changing the scan rate. The voltammograms for scan rates less than 0.5 V s⁻¹ were recorded on an X–Y recorder (Riken Denshi F42CP), and those at scan rates more than 0.5 V s⁻¹ were obtained with two transient recorders (Kawasaki Electronica TM-1410, 8-bit, 2K words for each one) as an X–Y recorder.

Controlled-potential electrolysis (CPE) was undertaken by using a two compartment cell with a fine glass frit. The working electrode was a platinum plate (ca. 150 cm²). After exhaustive electrolysis, 5 mL of water was added to the solution, the solution was concentrated to ca. 30 mL, 50 mL of water was added, and the product was extracted with chloroform. The crude product was chromatographically purified by using alumina (Wako B-10)–ethyl acetate and was recrystallized from ethanol. The product was 10-phenylphenothiazine 5-oxide (PPTZ(O)): mp 171–172.5 °C (lit.²⁰ mp 172–173 °C); mass spectrum, m/e 291 (M⁺; calcd for PPTZ(O) m/e 291.4 (M)); UV_{max} (MeCN) 233 nm (log ϵ 4.45), 276 (4.18), 302 (3.93), 338 (3.86); IR (KBr) 1040 cm⁻¹ (S=O). Anal. Calcd for C₁₈H₁₃NOS: C, 74.20; H, 4.50; N, 4.81. Found: C, 74.32; H, 4.63; N, 4.89. The yield of the product was more than 90% in the solution after electrolysis by both UV spectrometry and cyclic voltammetry, and the isolated yield by the above procedure was more than 60%.

As the supporting electrolyte, 0.5 M NaClO₄ was always used. The reference electrode was an Ag/AgClO₄ (0.01 M) couple in MeCN. The kinetic study was carried out at various temperatures between –20 and +35 °C within an accuracy of ±0.2 °C under an atmosphere of nitrogen. The electrochemical experiments were carried out at 25 °C unless otherwise specified.

Results and Discussion

Cyclic Voltammetry. Figure 1 shows cyclic voltammograms of PPTZ at various concentrations of water. At water concentrations of less than 3 mM, two reversible redox couples were observed at a scan rate of 0.2 V s⁻¹; for both waves I and II, the peak separations for the anodic and the corresponding re-reduction peaks, $E_{pa} - E_{pc}$, were 60 mV, and the peak current ratios, i_{pc}/i_{pa} , were unity. The anodic waves at $E_{pa} = 0.41$ and 1.10 V are, respectively, due to oxidation of PPTZ to its cation radical (PPTZ^{•+}) and dication (PPTZ²⁺). The introduction of a nitrogen atom causes the oxidation potential of PPTZ to be significantly less positive than that of TH ($E_{pla} = 0.86$ V). The equilibrium constant of disproportionation of the cation radical, $2PPTZ^{\bullet+} \rightleftharpoons PPTZ^{2+} + PPTZ$, is evaluated to be 2.2×10^{-12} at 25 °C²¹ from the difference in the peak potentials of waves I and II.¹⁰

When the water concentration was increased, wave II_a shifted to somewhat negative potentials, the corresponding re-reduction peak (II_c) disappeared, and new oxidation waves (III_a and IV_a) appeared at more positive potentials. The peak potential of wave III_a is also shifted to less positive potentials with an increase in the concentration of water. On the other hand, no appreciable change in potential and reversibility was observed for wave I at the

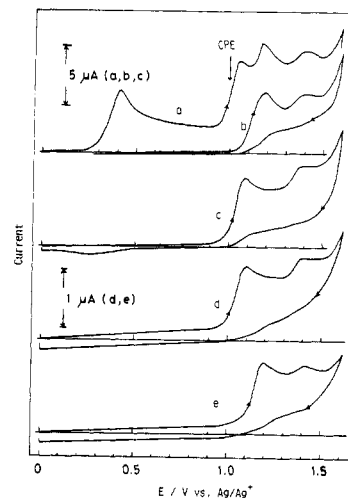


Figure 2. Cyclic voltammograms of 5 mM PPTZ (a–c) and of 1 mM PPTZ(O) (d and e) in MeCN–0.5 M NaClO₄ containing 45 mM water at 25 °C: a, before CPE at 1.0 V; b, after CPE at 1.0 V; c, after an excess water was added to the solution of b; d, 1 mM PPTZ(O); e, 1 mM PPTZ(O) with 10 mM perchloric acid (PPTZ(OH)⁺ was formed). The scan rate was 0.2 V s⁻¹.

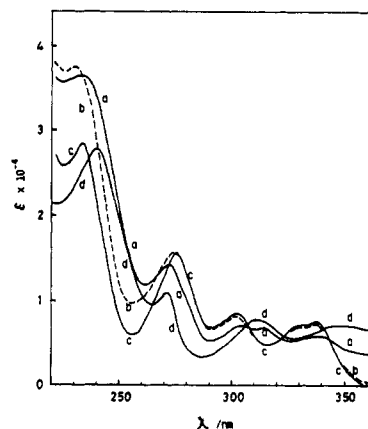


Figure 3. UV spectra: a, just after CPE of 1 mM PPTZ at 1.0 V in MeCN–0.5 M NaClO₄ containing 90 mM water; b, after an excess water was added to the solution of a ($[H_2O] > 1.0$ M); c, PPTZ(O) in dry MeCN (the spectrum was similar to that of c); d, PPTZ(O) in MeCN containing 10 mM perchloric acid (PPTZ(OH)⁺ was formed, and when sodium ion was added to this solution, the spectrum changed to one which is almost the same as that for a).

water concentrations up to at least 260 mM. Thus, the dication is far more electrophilic than the cation radical and reacted rapidly with water.

Controlled-Potential Electrolysis (CPE). To obtain the final product of the reaction of PPTZ²⁺ with water, we carried out CPE at 1.0 V²² for 1–5 mM PPTZ solutions containing 20–260 mM water. Two electrons (2.0 ± 0.1) per molecule of PPTZ were consumed for exhaustive electrolysis, and the solution turned light green; the color gradually became reddish green when the solution was allowed to stand. The voltammogram and the UV spectrum of the solution just after CPE was somewhat different from those of PPTZ(O), and, finally, by addition of excess water to the solution they became almost the same as those of PPTZ(O) (Figures 2 and 3). For clarification of the structure of the oxidation product of PPTZ in the solution, perchloric acid was added to a PPTZ(O) solution containing sodium perchlorate. The voltammogram (Figure

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(21) The equilibrium constants for the disproportionation obtained are 3.7×10^{-14} , 3.4×10^{-13} , 8.3×10^{-13} , and 4.3×10^{-12} at –20, 0, 15, and 35 °C, respectively.

(22) The sloping portion of the second oxidation wave was used to avoid further oxidation at the third wave.

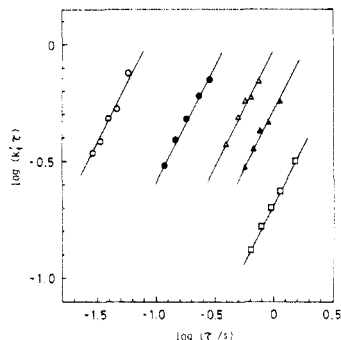


Figure 4. Plots of $\log k_f' \tau$ vs. $\log \tau$ at 15 °C at various concentrations of water: \square , 3.0 mM; \blacktriangle , 6.1 mM; \triangle , 9.6 mM; \bullet , 12.7 mM; \circ , 31.9 mM. The slope of the lines is 1.0.

2) and the UV spectrum (Figure 3) of the solution thus obtained were the same as those observed just after CPE. Furthermore, on irradiation of the solution with either UV light or sunlight, a reddish orange color developed, and PPTZ⁺ (UV-vis_{max} in MeCN: 274, 315, 515, 770, and 860 nm) was generated; similar results were reported²³ for 5-hydroxyphenothiazinium ion in acidic solutions. Thus, the oxidation product of PPTZ in the solution must be 5-hydroxy-10-phenylphenothiazinium ion (PPTZ(OH)⁺). The PPTZ(OH)⁺ solution obtained by adding perchloric acid to a PPTZ(O) solution itself was colorless, but when sodium ion was present in the solution, it turned light green; the UV spectrum was also changed (Figure 3). However, the reason for this coloration by an interaction between sodium ion and PPTZ(OH)⁺ is still unknown.²⁴ Thus, PPTZ²⁺ reacted with water to form PPTZ(OH)⁺ which is further deprotonated by an excess of water to give PPTZ(O). When the solution was allowed to stand after two-electron oxidation of PPTZ, PPTZ⁺ was formed from PPTZ(OH)⁺ with the aid of daylight and the solution became reddish green.

Kinetic Study. To obtain more precise information regarding mechanism of the reaction of the dication with water, we carried out kinetic investigations. Since the cation radical is completely inactive at the water concentrations used during the time scale of voltammetric measurement, the decay of the dication in the vicinity of the electrode can be given in eq 1, where k_f is the rate constant

$$-d[\text{PPTZ}^{2+}]/dt = k_f[\text{PPTZ}^{2+}]^n[\text{H}_2\text{O}]^m \quad (1)$$

of the reaction of the dication with water. The water concentrations used in the present study seem to be in excess with respect to the amount of the dication which is produced at the electrode during a voltammetric measurement, and thus, in the case where $n = 1$ in eq 1, pseudo-first-order decay of the dication is expected (eq 2 and 3).

$$-d[\text{PPTZ}^{2+}]/dt = k_f'[\text{PPTZ}^{2+}] \quad (2)$$

$$k_f' = k_f[\text{H}_2\text{O}]^m \quad (3)$$

Thus, the values of $\log k_f' \tau$ (see Experimental Section for τ) were calculated from the peak current ratios for wave II, $i_{p\text{II}_c}/i_{p\text{II}_a}$, according to Nicholson and Shain¹⁹ for the following reaction scheme: $\text{R} \rightleftharpoons \text{O} + e$, $\text{O} \rightarrow \text{Z}$ (so-called an EC mechanism).^{9,19} At a given water concentration, the plots of $\log k_f' \tau$ vs. $\log \tau$ showed a good straight line with

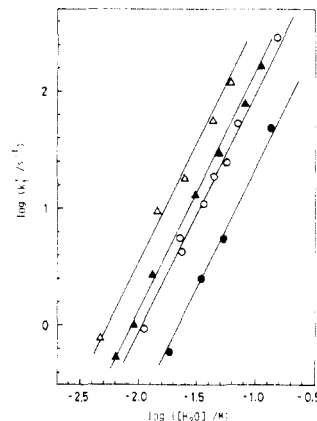


Figure 5. Plots of $\log k_f'$ vs. $\log [\text{H}_2\text{O}]$ at various temperatures: \bullet , -20 °C; \circ , 0 °C; \blacktriangle , 15 °C; \triangle , 35 °C. The slope of the lines is 2.0.

Table I. Kinetic Parameters for the Reaction of PPTZ²⁺ with Water

temp, ^a °C	reaction order with respect to $[\text{H}_2\text{O}]^c$	$\log k_f^b$
-20	2 ± 0.2	3.34 ± 0.05
0	2 ± 0.2	3.96 ± 0.07
15	2 ± 0.2	4.11 ± 0.07
25	1.8 ± 0.3	4.38 ± 0.10
35	1.8 ± 0.3	4.57 ± 0.10

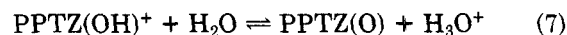
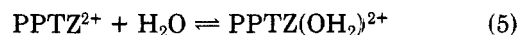
^a Within an accuracy of ± 0.2 °C. ^b Calculated from eq 4 for $m = 2$. The units of k_f are $\text{M}^{-2} \text{s}^{-1}$. ^c The reaction order was 1 with respect to $[\text{PPTZ}^{2+}]$ in all cases.

a slope of 1.0 (± 0.1); that is, a constant value for k_f' was obtained (Figure 4). Similar results were obtained at the other temperatures tested. This indicates that the dication diminished in a pseudo-first-order manner with respect to the concentration of the dication ($n = 1$ in eq 1) and that the method used here is applicable to the kinetic study. The values of $\log k_f'$ were obtained from both calculation ($\log k_f' \tau - \log \tau$) and the intercept at $\log \tau = 0$ in Figure 4 (when necessary, the line was extrapolated to $\log \tau = 0$ by the least-squares method). Then the values of $\log k_f'$ thus obtained at various concentrations of water were plotted against the water concentration as $\log [\text{H}_2\text{O}]$ (Figure 5). A linear relationship with a slope of ca. 2 was obtained at various temperatures (Table I). Since eq 3 gives eq 4, the plot of $\log k_f'$ vs. $\log [\text{H}_2\text{O}]$ gives the values

$$\log k_f' = \log k_f + m \log [\text{H}_2\text{O}] \quad (4)$$

of m and $\log k_f$ by the slope of the line and the intercept at $\log [\text{H}_2\text{O}] = 0$, respectively (Figure 5). Also, the values of $\log k_f$ were calculated from eq 4 at given concentrations of water for $m = 2$; the data are summarized in Table I.

The rate law of the reaction of interest is, therefore, first and second order in the concentrations of the dication and water, respectively. To account for this rate law and the results of CPE, we propose the pathway given by eq 5–7.



A plot of $\log(k_f/T)$ vs. $1/T$, the Eyring plot (not shown), where k_f is the rate constant at absolute temperature T , from the data in Table I yields the activation enthalpy $\Delta H^\ddagger = 30.5 \text{ kJ/mol}$ (7.3 kcal/mol) from the slope of the line and the activation entropy $\Delta S^\ddagger = -58.5 \text{ J/(mol K)}$ (-14 eu)

(23) H. J. Shine and E. E. Mach, *J. Org. Chem.*, 30, 2130 (1965).

(24) Neither a color change nor an appreciable change in the UV spectrum was observed when a tetra-*n*-butylammonium perchlorate crystal was added to a PPTZ(OH)⁺ solution. Both PPTZ(O) and HClO₄ solutions containing either NaClO₄ or Bu₄NClO₄ had no color. Also, no significant effect of water was observed. Thus, the color is due to an interaction between PPTZ(OH)⁺ and Na⁺.

Table II. Activation Parameters^a for the Reaction of PPTZ²⁺ with Water

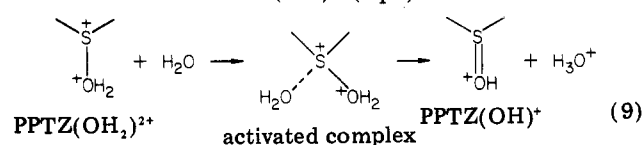
A, s^{-1}	$E_a, kJ mol^{-1}$	$\Delta H^\ddagger, kJ mol^{-1}$	$\Delta S^\ddagger, J mol^{-1} K^{-1}$	$\Delta G^\ddagger, kJ mol^{-1}$
1.4×10^{10}	32.6 (7.8) ^d	30.5 ^c (7.3) ^d	-58.5 (-14) ^e	48.1 (11.5) ^d

^a The values of E_a and ΔH^\ddagger were estimated from the slopes of the Arrhenius plot and the Eyring plot, respectively, by using the least-squares method, whereas the values of A and ΔS^\ddagger were obtained from the intercept at $1/T = 0$. The values of ΔS^\ddagger were also calculated by using eq 8 at various temperatures; the mean value of ΔS^\ddagger thus obtained was almost the same as that given in the table. ^b At 25 °C. ^c $E_a - RT$ at 25 °C is 30.1 kJ mol⁻¹ (7.2 kcal mol⁻¹). ^d These values are in units of kcal mol⁻¹. ^e This value is in entropy units.

from the intercept at $1/T = 0$. Similar values of ΔS^\ddagger were obtained by substituting the values of k_f and ΔH^\ddagger at given temperatures into eq 8, where k , h , and R are, respectively,

$$k_f = \frac{kT}{h} \exp\left[-\frac{\Delta H^\ddagger}{RT}\right] \exp\left[\frac{\Delta S^\ddagger}{R}\right] \quad (8)$$

Boltzmann's constant, Planck's constant, and the gas constant. The activation energy, E_a , and frequency factor, A , obtained from the Arrhenius plot (not shown) are also given in Table II. The negative value of ΔS^\ddagger is consistent with the notion that the activation step is the nucleophilic attack of water on PPTZ(OH₂)²⁺ followed by fast deprotonation to form PPTZ(OH)⁺ (eq 9). A similar reaction



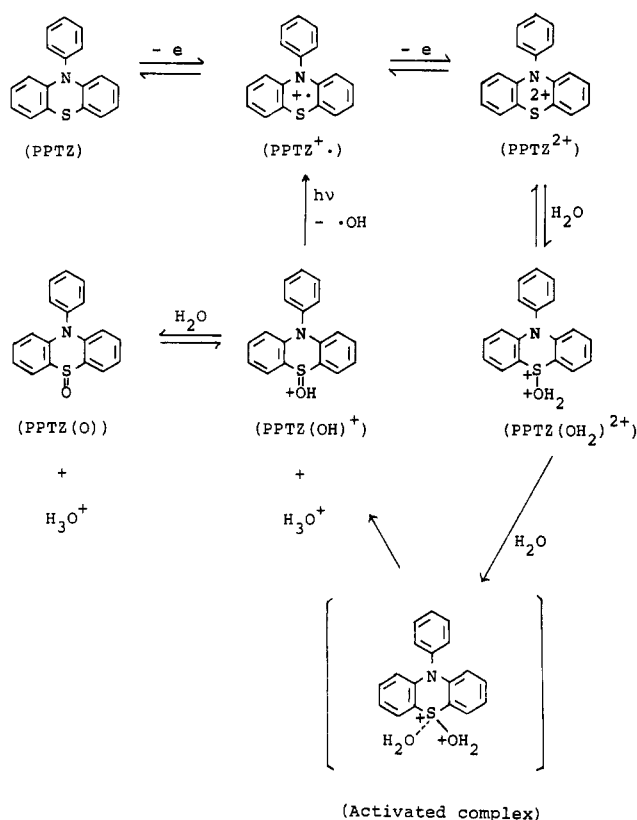
pathway to that proposed above was suggested¹² for hydrolysis of the dicationic pyridinium adducts which were formed by the HRM of cation radicals of TH and PPTZ. Thus, the stepwise attack of nucleophiles to a dicationic species in nucleophilic addition seems to be a rather usual reaction pathway.

The reactivity of PPTZ²⁺ and related dications can be explained as follows. Thianthrene dication (TH²⁺) is far more reactive than PPTZ²⁺; in the cyclic voltammogram of 1 mM TH, no return peak for the second wave was observed in almost dry (5 mM water) acetonitrile at 0.2 V s⁻¹. Since the presence of the nitrogen atom makes the energy level of the LUMO of PPTZ²⁺ higher than that of TH²⁺,²⁵⁻²⁷ TH²⁺ is more reactive as an electron acceptor

(25) The observed oxidation potentials can be used as a measure of the energy levels of MO's. The anodic peak potentials observed for acetonitrile solutions of 1 mM PTZ, PPTZ, and TH were, respectively, 0.29, 0.41, and 0.86 V for the first wave and 0.75, 1.1, and 1.3 V for the second wave. Thus, the energy levels of the HOMO are in the order PTZ > PPTZ > TH. Since cationic species would be formed by removing electrons from the HOMO of the precursors, the energy levels of the HOMO's of the precursors become those of the LUMO's of the corresponding cationic species. Thus, TH²⁺, whose energy level of LUMO is lower than that of PPTZ²⁺, is a stronger electron acceptor than PPTZ²⁺.

(26) It has been reported,²⁷ for example, that the first and the second ionization potentials of phenothiazine and its derivatives, from photoelectron spectra of these compounds, are in good agreement with the energy levels calculated for the highest and the second highest occupied MO's which are most heavily N lone pair and S lone pair in character, respectively.

Scheme I



than PPTZ²⁺. In the case of the nucleophilic attack by water on PPTZ²⁺, electrons donated from water would be accepted by two different orbitals,²⁶ the first electron is easily accepted by the orbital of lower energy level, while the second electron transfer would occur at a higher energy level, and thus, the attack of the second water on PPTZ(OH₂)²⁺ to form PPTZ(OH)⁺ becomes rate determining. On the other hand, the attack of the second water on the corresponding TH(OH₂)²⁺, even if TH(OH₂)²⁺ is assumed to be formed, is still fast because the energy level of the LUMO of TH(OH₂)²⁺ would be lower than that of PPTZ(OH₂)²⁺,^{25,26} thus, TH²⁺ reacts rapidly with water to form thianthrene 5-oxide. For phenothiazine (PTZ) whose second wave is still fairly reversible in a solution containing 100 mM water at the scan rate of 0.2 V s⁻¹, the dication (PTZ²⁺) is stabilized by the presence of an N atom,^{25,26} as in the case of PPTZ, and, furthermore, the positive charge removal via proton release at the nitrogen atom.

As is described in this paper, a well-known cyclic voltammetric technique can be successfully applied to a kinetic study of a dication under appropriate conditions, and this method is useful because no isolated dication as a reactant (which is very difficult to prepare) is needed.

The reaction pathways described in this paper are summarized in Scheme I.

Registry No. PPTZ, 7152-42-3; PPTZ(O), 23099-78-7; PPTZ²⁺, 56301-73-6.

(27) L. N. Domelsmith, L. L. Munchausen, and K. N. Houk, *J. Am. Chem. Soc.*, **99**, 6506 (1977).