Reactions of Cation Radicals of EE Systems. 6. The Pyridination of 10-Phenylphenothiazine: Heteroatom Effects on Rates and Mechanisms of Pyridinations[1]

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The kinetics of the reaction of 10-phenylphenothiazine (PH) cation radical ($PH^{\cdot+}$) with pyridine (Py) have been examined. Electrochemical characterization of the $PH/PH^{\cdot+}$ couple in neat Py showed $PH^{\cdot+}$ to be of sufficiently low reactivity to permit kinetic investigation in this medium. The results of these kinetic determinations, together with those obtained in acetonitrile solutions of Py, indicate the applicability of a half-regeneration mechanism. The reaction gives rise to only the pyridinated product in neat Py while both hydrolysis (sulfoxide) and pyridination products are observed in acetonitrile solutions. Formation of the sulfoxide is accounted for by the hydrolysis of an N–S bonded dicationic intermediate in the proposed pyridination mechanism. The product distributions observed in the pyridinations of the cation radicals derived from PH and other EE substrates reflect the relative reactivities of the corresponding dicharged intermediates.

A half-regeneration mechanism[2] has been shown to be tenable for the reaction of pyridine with thianthrene cation radical ($Th^{\cdot+}$) in acetonitrile.[1a] Although this reaction afforded thianthrene 5-oxide rather than the *N*-(2-thianthrenyl)pyridinium ion formed in neat pyridine,[3] the rate of radical ion consumption was nonetheless first order in pyridine concentration.[1a] It was concluded that the N–S bond in the oxidized form of the pyridine adduct of thianthrene cation radical was hydrolyzed by residual water present in the acetonitrile.[1a] The mechanism by which the pyridinated product is formed in neat pyridine was not elucidated owing to the high reactivity of the cation radical in this medium.[3]

Reactions of phenothiazine cation radical with neat pyridine have been shown to afford product types and distributions similar to those noted in the case of thianthrene.[3] Since the presence of the nitrogen heteroatom diminishes the reactivity of the sulfur site in the cation radical, it was envisioned that the pyridination of phenothiazine would proceed more slowly, thereby permitting convenient mechanistic investigation. Moreover, this examination would allow the comparison of mechanisms by which carbon centered,[4,5] sulfur centered,[1a] and mixed nitrogen–sulfur centered cation radicals of EE systems react with pyridine.

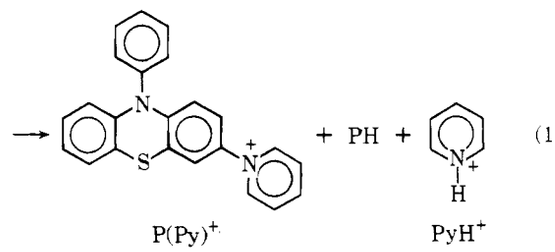
The chemistry of the phenothiazine cation radical is, however, complicated by the ease with which it may be deprotonated.[6] The free radical resulting from this deprotonation dimerizes and undergoes further oxidation.[3,7-9] Such a reaction sequence represents a pathway for the consumption of cation radical which is parallel to and competes with the nucleophilic addition/substitution reactions which are of primary interest in this study. To circumvent these complications so that this present investigation might focus on the nucleophile/cation radical reaction, the *N*-phenyl substituted phenothiazine (PH) was chosen as a representative dibenzenoid EE system containing both nitrogen and sulfur heteroatoms.

This paper reports the electrochemical and spectroscopic characterization of the reaction dynamics of 10-phenylphenothiazine cation radical ($PH^{\cdot+}$) in both neat pyridine and pyridine/acetonitrile solutions. Together with product characterizations, these results provide the basis for a general mechanism which accounts for the kinetics and product distributions observed for the two sulfur-containing EE systems, thianthrene[1a,3] and 10-phenylphenothiazine, in reactions with Py.

Results and Discussion

The anodic voltammetric behavior of PH at platinum in acetonitrile under conditions of slow potential scan (0.10 V s^{-1}) is shown in Figure 1A. The wave at O_1 (+0.68 V) corresponds to the oxidation of PH to $PH^{\cdot+}$ and the wave at O_2 (+1.37 V) results from further oxidation of $PH^{\cdot+}$ to the dication, PH^{2+}. The dication is not sufficiently stable in this medium to be detected upon scan reversal at this rate of potential sweep.[10] At higher scan rate (20 V s^{-1}), the reduction of the dication in the same solvent-supporting electrolyte system is readily observed (R_2, Figure 1B).

Stoichiometry of the $PH^{\cdot+}$/Py Reaction. The perchlorate salt of $PH^{\cdot+}$, prepared after the manner of Shine,[3] was reacted in neat pyridine and afforded stoichiometric quantities of *N*-[3-(10-phenylphenothiazinyl)]pyridinium perchlorate,[12] phenothiazine, and pyridinium perchlorate (eq 1). These reaction products are exactly analogous to those observed for the reactions of the perchlorate salts of the cation radicals of both thianthrene and unsubstituted phenothiazine in neat pyridine.[3]



(1)

The electrooxidation (+0.80 V) of PH in acetonitrile solutions of pyridine show the release of two Faradays of charge per mole of PH consumed and gives rise to the formation of both $P(Py)^+$ and 10-phenylphenothiazine 5-oxide [PH(O)] in addition to PH and PyH^+. The formation of PH(O) in this medium (eq 2)

$$2PH^{\cdot+} + 2Py + H_2O \rightarrow PH(O) + PH + 2PyH^+ \quad (2)$$

is analogous to the formation of thianthrene 5-oxide from the corresponding cation radical under similar reaction conditions.[1a]

The voltammetry of $P(Py)^+$, isolated as the perchlorate salt from reactions in both neat Py and acetonitrile solutions of

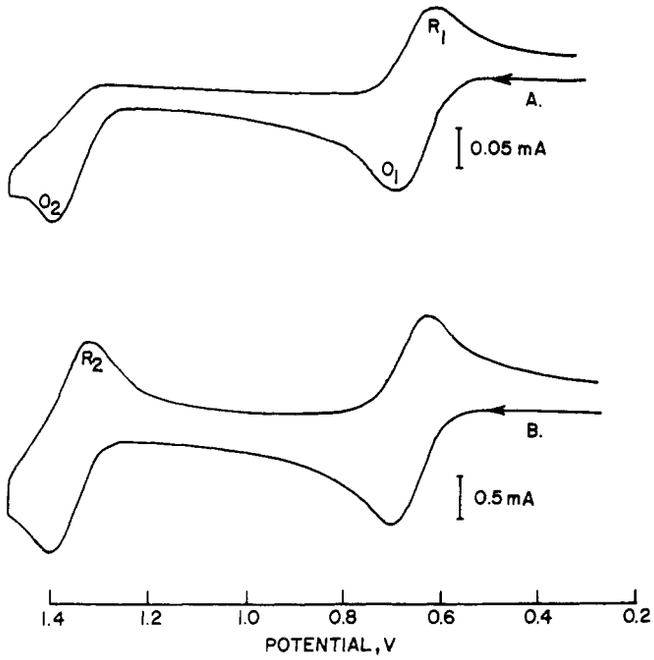


Figure 1. Cyclic voltammetric behavior of PH at a platinum electrode (0.36 cm^2) in acetonitrile containing TEAP. (A) [PH] = 1.0 mM, [TEAP] = 0.10 M, sweep rate 0.10 V s^{-1}; (B) [PH] = 1.1 mM, [TEAP] = 0.20 M, sweep rate 20 V s^{-1}.

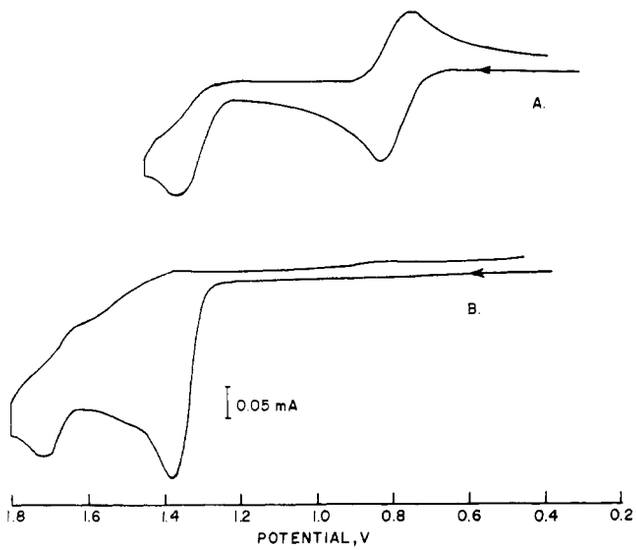


Figure 2. Cyclic voltammetric behavior of 1.0 mM (A) $P(Py)^+$ and (B) PH(O) at a platinum electrode (0.3 cm^2) in acetonitrile containing 0.10 M TEAP, sweep rate 0.10 V s^{-1}.

Py, is shown in Figure 2A. The monoelectronic oxidation wave at +0.81 V corresponds to the reversible formation of a dication radical (eq 3).

$$P(Py)^+ \rightleftharpoons P(Py)^{\cdot 2+} + e^- \quad (3)$$

As expected, the oxidation potential of the pyridinium substituted 10-phenylphenothiazine is observed to be anodic of that observed for PH.[13]

The voltammetry of PH(O), isolated from the reaction in acetonitrile, is shown in Figure 2B. This electrochemical behavior is identical with that observed for authentically prepared PH(O).[15] From the voltammetry shown in Figure 2, it can be seen that the formation of $P(Py)^+$ could be monitored electrochemically during the reaction of $PH^{\cdot +}$ with Py. This was not the case for PH(O) since its oxidation potential occurs

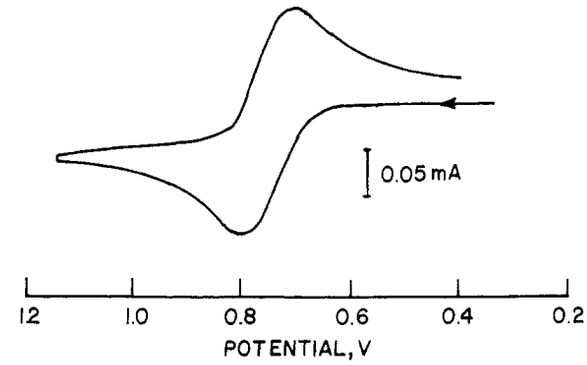


Figure 3. Cyclic voltammetric behavior of 1.0 mM PH at a platinum electrode (0.36 cm^2) in neat Py containing 0.10 M TEAP, sweep rate 0.10 V s^{-1}.

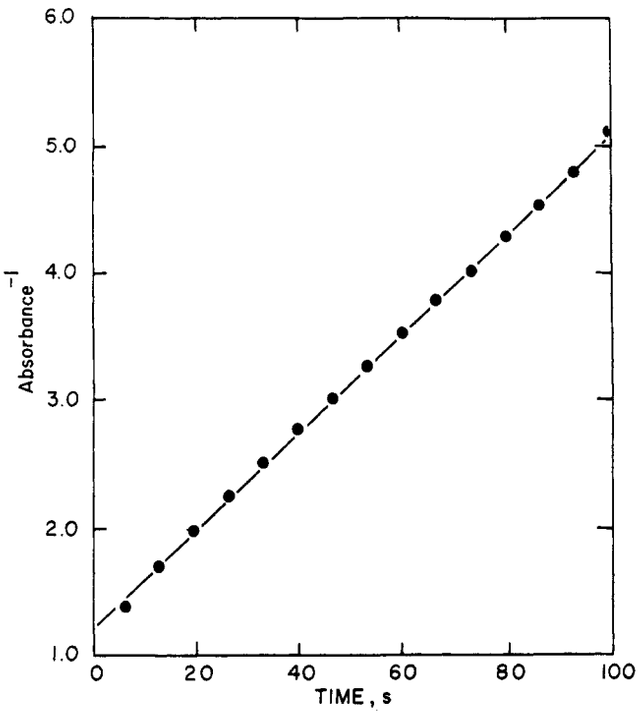


Figure 4. Second-order kinetic plot for reaction of $PH^{\cdot +}$ in neat Py. $[PH^{\cdot +}]_0 = 1.02 \times 10^{-4}$ M, $[PH]_0 = 5.0 \times 10^{-3}$ M, slope = 3.90 (± 0.03) $\times 10^{-2}$ A^{-1} s^{-1}, coefficient of correlation = 0.9997.

more anodically than that of Py. Isolation of PH(O) from the acetonitrile reaction mixture showed it and $P(Py)^+$ to be found in approximately a 1:3 ratio.

The Reaction in Neat Pyridine. The low reactivity of $PH^{\cdot +}$ toward Py is indicated by the voltammetry of the $PH/PH^{\cdot +}$ couple *in neat pyridine* shown in Figure 3. In this medium, the disappearance of $PH^{\cdot +}$ proceeds with a seond-order dependence on cation radical concentration (Figure 4). The apparent pseudo-second-order rate constant, k_{app}, for this process was found to be inversely dependent on precursor (PH) concentration in the manner shown in Figure 5. These data are of the form

$$1/k_{app} = C_1[PH] + C_2 \quad (4)$$

and afford linear regression values of 4.38 (±0.03) $\times 10^{-1}$ s and 1.37 (± 0.27) $\times 10^{-3}$ M s for C_1 and C_2 (eq 4), respectively. The kinetics of this reaction are then appropriately described by

$$-\frac{d[PH^{\cdot +}]}{dt} = \left(\frac{2.28}{[PH] + 3.13 \times 10^{-3}}\right)[PH^{\cdot +}]^2 \quad (5)$$

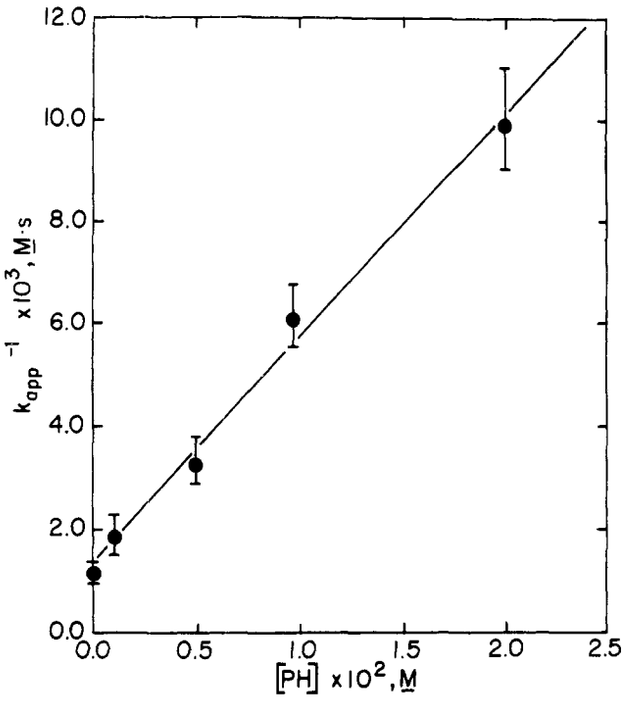


Figure 5. Dependence of the apparent pseudo-second-order rate constant on [PH] for the reaction of PH·$^+$ in neat Py. Vertical bars indicate $\pm 1\sigma$ in k_{app}. Solid line from linear regression (eq 4); coefficient of correlation = 0.985.

The second-order dependence of rate on cation radical concentration and inverse first-order dependence on neutral precursor concentration together with the observed stoichiometry suggests the involvement of a disproportionation step[16] (eq 6) prior to rate-determining encounter of dication with Py.

Scheme I

$$PH^{\cdot+} + PH^{\cdot+} \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} PH^{2+} + PH \quad (6)$$

$$PH^{2+} + Py \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} PH(Py)^{2+} \quad (7)$$

$$PH(Py)^{2+} + Py \xrightarrow{k_8} P(Py)^{+} + PyH^{+} \quad (8)$$

Assuming that the disproportionation step is fast and reversible and that the rate-determining attack of nucleophile on dication (eq 7) is irreversible, one derives an expression for the disappearance of cation radical given by eq 9.

$$-\frac{d[PH^{\cdot+}]}{dt} = \frac{2k_7K_{dis}[PH^{\cdot+}]^2[Py]}{[PH]} \quad (9)$$

While the appropriate reaction orders for PH·$^+$ and PH are embodied in eq 9, this rate law predicts that a plot of $1/k_{app}$ vs. PH concentration should afford a straight line with a *zero intercept* (i.e., from eq 4, $C_1 = \frac{1}{2}k_7K_{dis}[Py]$, $C_2 = 0$). Clearly the intercept of Figure 5 is nonzero. Moreover, if one assumes that some systematic error in the kinetic analyses gave rise to the nonzero intercept of Figure 5 and then proceeds to evaluate k_7 from the slope of this plot, a value of 4.18 ($\pm$0.03) $\times$ 10^{10} M^{-1} s^{-1} is calculated. This value of k_7 exceeds the diffusion controlled rate constant (k_{diff}) in pyridine which is estimated[17] to be 7.4×10^9 M^{-1} s^{-1}. Clearly Scheme I, constrained by the assumptions outlined above, does not adequately account for the observed data.

If it is again assumed that the attack by nucleophile on dication (eq 7) is irreversible and rate determining but that the disproportionation process (eq 6) is not a rapidly established equilibrium, then application of steady-state kinetics to [PH^{2+}] affords the rate expression

$$-\frac{d[PH^{\cdot+}]}{dt} = \frac{k_6k_7[Py]}{k_{-6}[PH] + k_7[Py]}[PH^{\cdot+}]^2 \quad (10)$$

from which

$$\frac{1}{k_{app}} = \frac{k_{-6}[PH]}{k_6k_7[Py]} + \frac{1}{k_6} \quad (11)$$

From the numerical value of $1/k_6$ (the intercept of Figure 5) and the experimentally determined value of K_{dis},[16] k_{-6} is evaluated to be 3.3 ($\pm$0.6) $\times$ 10^{14} M^{-1} s^{-1}, *which is in excess of the diffusion limit.* Even if the comproportionation reaction (the reverse of eq 6) were diffusion controlled, no linear dependence of k_{app} on [PH] would be observed.

A third possibility is that eq 6 is a rapidly established, reversible equilibrium and eq 7 is a reversible equilibrium or pseudoequilibrium process. Taking eq 8 to be rate determining yields the rate expression given by eq 12.

$$-\frac{d[PH^{\cdot+}]}{dt} = \frac{2k_8K_7K_{dis}[PH^{\cdot+}]^2[Py]^2}{[PH]} \quad (12)$$

Like eq 9, this rate law does not account for the experimental observations in that it predicts a *zero intercept* for a plot of $1/k_{app}$ vs. [PH].

A fourth possibility is that the disproportionation step (eq 6) is a rapidly established equilibrium, eq 7 is reversible, and the rates of reactions 7 and 8 are of comparable magnitudes such that neither is rate determining. With these stipulations, steady-state kinetics can be applied to [$PH(Py)^{2+}$], giving rise to the rate expression given in eq 13.

$$-\frac{d[PH^{\cdot+}]}{dt} = \frac{2k_7k_8K_{dis}[PH^{\cdot+}]^2[Py]^2}{(k_8[Py] + k_{-7})[PH]} \quad (13)$$

This form is also unacceptable in that it, too, predicts a *zero intercept* for a plot of $1/k_{app}$ vs. [PH].

Lastly, the possibility that both the disproportionation process (eq 6) and the addition of Py to the dication (eq 7) are not rapidly established equilibria must be addressed. If no reactive intermediates build up, then application of steady-state kinetics to *both* [PH^{2+}] and [$PH(Py)^{2+}$] affords the rate expression

$$-\frac{d[PH^{\cdot+}]}{dt} = \frac{2k_6k_7k_8[PH^{\cdot+}]^2[Py]^2}{k_{-6}[PH](k_{-7} + k_8[Py]) + k_7k_8[Py]^2} \quad (14)$$

for which

$$\frac{1}{k_{app}} = \frac{k_{-6}(k_{-7} + k_8[Py])}{2k_6k_7k_8[Py]^2}[PH] + \frac{1}{2k_6} \quad (15)$$

Under these constraints a plot of $1/k_{app}$ vs. [PH] yields a nonzero intercept. However, the numerical value of k_{-6}, calculated from the intercept of Figure 5 and the experimentally determined value of K_{dis}[16] to be 1.7 ($\pm$.0.3) $\times$ 10^{14} M^{-1} s^{-1}, is in *excess of the diffusion limit.*

An alternative to the disproportionation pathway is the half-regeneration mechanism,[2] Scheme II, which retains the proper overall stoichiometry.

Scheme II

$$PH^{\cdot+} + Py \underset{k_{-16}}{\overset{k_{16}}{\rightleftharpoons}} PH(Py)^{\cdot+} \quad (16)$$

$$PH(Py)^{\cdot+} + PH^{\cdot+} \underset{k_{-17}}{\overset{k_{17}}{\rightleftharpoons}} PH(Py)^{2+} + PH \quad (17)$$

$$PH(Py)^{2+} + Py \xrightarrow{k_{18}} P(Py)^{+} + PyH^{+} \quad (18)$$

The required dependencies of reaction rate on PH·$^+$ and PH concentrations may be shown to arise from treatment of

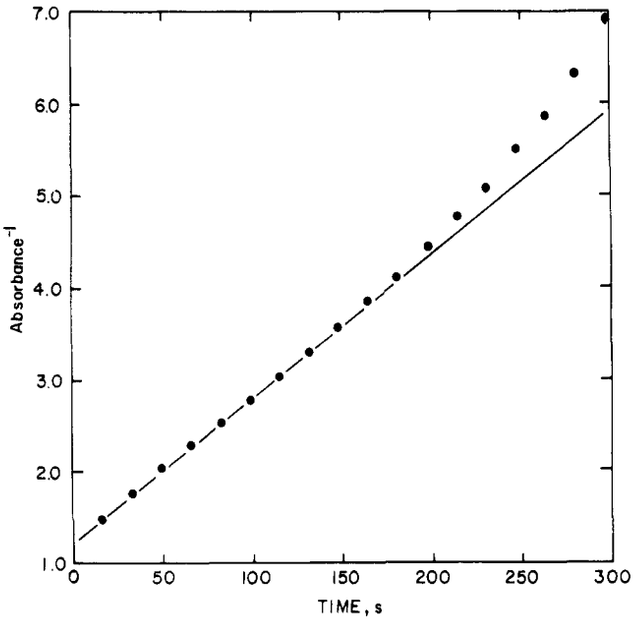


Figure 6. Representative kinetic plot for the reaction of $PH^{\cdot+}$ with Py in acetonitrile. $[PH^{\cdot+}]_0 = 1.00 \times 10^{-4}$ M, [Py] = 7.45 M, $[PH]_0$ = 0.00 M. For first half-life: slope = 1.55 (± 0.01) × 10^{-2} A^{-1} s^{-1}; coefficient of correlation = 0.9998.

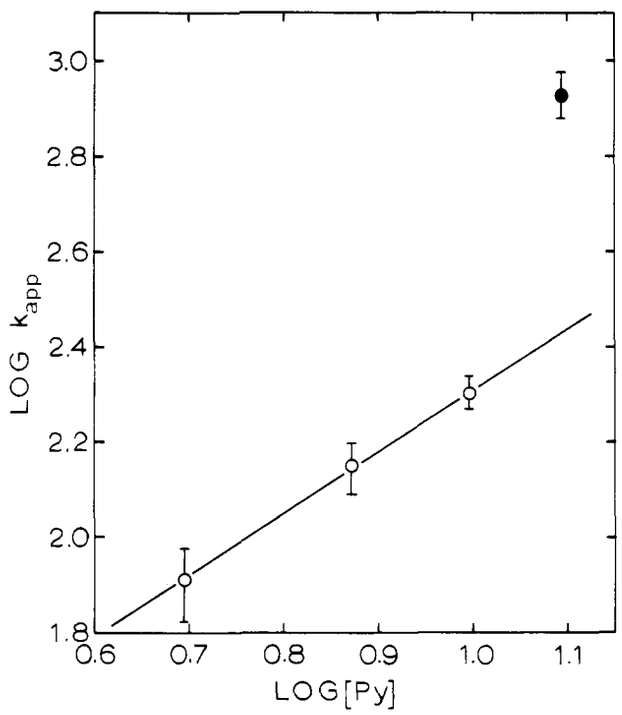


Figure 7. Dependence of the apparent rate constant (eq 20) for the reaction of $PH^{\cdot+}$ with Py on [Py]. Regression line for data obtained in acetonitrile/pyridine mixture (open circles), slope = 1.30 (± 0.04), coefficient of correlation = 0.9989. Solid circle is for reaction in neat Py (see text). $[PH]_0$ = 0.00 M in all cases.

the kinetic equations describing Scheme II provided that (1) the adduction equilibrium between $PH^{\cdot+}$ and Py (eq 16) is fast, (2) the electron transfer step (eq 17) is fast and reversible, and (3) steady-state kinetics may be applied to the concentration of the $PH(Py)^{2+}$ species. Under these conditions, eq 18 [deprotonation of $PH(Py)^{2+}$] is rate determining and eq 19 may be derived for the disappearance of $PH^{\cdot+}$.

$$-\frac{d[PH^{\cdot+}]}{dt} = \frac{2k_{16}k_{17}k_{18}[PH^{\cdot+}]^2[Py]^2}{k_{-16}(k_{-17}[PH] + k_{18}[Py])} \quad (19)$$

A *nonzero* intercept is predicted here for the data treatment of Figure 5.

Scheme II is offered as a tenable mechanism for this reaction.[20] The form of k_{app} (eq 4) becomes

$$k_{app} = \frac{2k_{16}k_{17}k_{18}[Py]^2}{k_{-16}(k_{-17}[PH] + k_{18}[Py])} \quad (20)$$

The slope (C_1, eq 4) of this plot may be assigned to the expression

$$C_1 = \frac{k_{-16}k_{-17}}{2k_{16}k_{17}k_{18}[Py]^2} = 4.38\ (\pm 0.03) \times 10^{-1}\ s \quad (21)$$

and the intercept (C_2, eq 4) to

$$C_2 = \frac{k_{-16}}{2k_{16}k_{17}[Py]} = 1.37\ (\pm 0.27) \times 10^{-3}\ M\ s \quad (22)$$

From these results and the concentration of neat Py (12.4 M) the kinetic parameters $k_{16}k_{17}k_{18}/k_{-16}k_{-17}$ and $k_{16}k_{17}/k_{-17}$ evaluate to 7.41 (±0.16) × 10^{-3} M^{-1} s^{-1} and 2.94 (±0.60) × 10^{-1} M^{-2} s^{-1}, respectively.

The Reaction in Acetonitrile Solutions. From eq 19, it can be seen that the dependence of reaction rate on Py concentration is bounded by the relative magnitudes of the two parenthetical denominator terms, $k_{-17}[PH]$ and $k_{18}[Py]$. In the limit of $k_{-17}[PH] \gg k_{18}[Py]$, a second-order dependence of reaction rate on Py concentration is predicted. In the other limit, i.e., $k_{-17}[PH] \ll k_{18}[Py]$, a first-order dependence should be observed. If the magnitudes of $k_{-17}[PH]$ and $k_{18}[Py]$ are similar, then an intermediate apparent reaction order is expected.

To evaluate the dependence of reaction rate on Py concentration, kinetic determinations were carried out in acetonitrile solutions containing various concentrations of Py. In this medium, however, multiple reaction pathways contribute to the consumption of cation radical and hence to complex observed kinetics.

The data presented in Figure 6 are typical of kinetic experiments conducted in this mixed solvent system. Although deviation from second-order dependence is reflected at sufficiently long times of observation, the initial rate of reaction is clearly dependent on $PH^{\cdot+}$ concentration in a second-order fashion. This is true for at least the first half-life. The dependence of this initial rate of reaction on concentration of Py in this solvent system, shown in Figure 7, is that predicted by eq 19, wherein $k_{-17}[PH]$ and $k_{18}[Py]$ are of similar magnitudes. That the apparent rate constant noted in neat Py is considerably higher than predicted from this figure is most probably a manifestation of the gross change in solvent character.[21]

The competing reaction in the acetonitrile solvent system is the formation of PH(O). This occurs via hydrolysis of $PH(Py)^{2+}$, this reaction being competitive with the deprotonation step in Scheme II (eq 18).

$$PH(Py)^{2+} + H_2O \rightarrow PH(OH)^+ + PyH^+ \quad (23)$$

$$PH(OH)^+ + Py \rightarrow PH(O) + PyH^+ \quad (24)$$

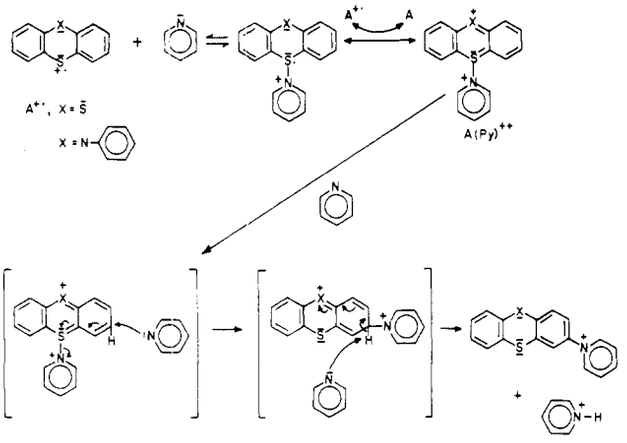
The hydrolysis of $PH(Py)^{2+}$ observed here is analogous to that noted in the reaction of thianthrene cation radical ($TH^{\cdot+}$) with Py in acetonitrile.[1a] In the $Th^{\cdot+}$ case, the hydrolysis of the analogous dicharged intermediate, $Th(Py)^{2+}$, proceeds with complete exclusion of pyridination. The relative reactivity of $PH(Py)^{2+}$ toward water is much less, however, and in this case the formation of both $P(Py)^+$ and PH(O) is observed. In fact, if hydrolysis of $PH(Py)^{2+}$ were the dominant pathway, then a first-order dependence of initial rate on Py concentration would be expected. Both the data shown in Figure 7 and the

product distribution reflect the initial dominance of the pyridination rather than the hydrolysis process.

Conclusions

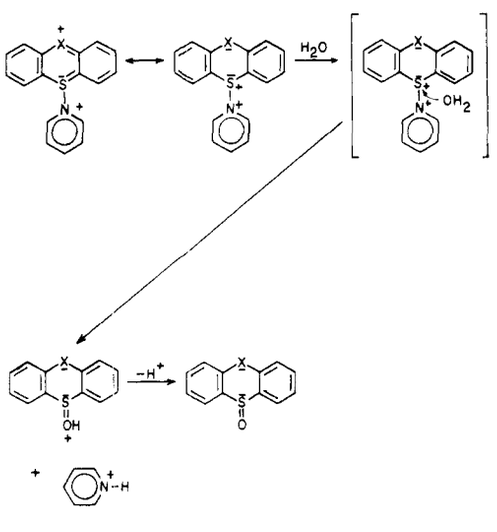
While it is known that the pyridinations of the cation radicals of thianthrene and phenothiazine[3] give rise to nucleophilic *substitution* products (carbon ring site), it is also established that the reactions of the cation radicals of thianthrene, 10-methylphenothiazine, and 10-phenylphenothiazine with protic nitrogen centered nucleophiles (viz., ammonia,[24] primary and secondary amines[25,26]) afford nucleophilic *addition* products (sulfur site). That pyridine should behave in this anomalous way toward sulfur-containing cation radicals is explicable in terms of the necessary product stability attainable through charge relief via release of protons borne by the nitrogen centered nucleophile.[3] Such stabilization has been found to be unnecessary in the case of the carbon centered 9,10-diphenylanthracene cation radical ($DPA^{\cdot+}$) in reaction with Py and triethylamine.[5]

The formation of thianthrene 5-oxide (ThO)[1a,3] and PH(O) in the course of the reaction of the respective cation radicals with pyridine, together with the observation that the rate of ThO formation is proportional to Py concentration, leads to the conclusion that the initial encounter of Py with these sulfur-centered cation radicals occur *at a sulfur site*. The following general mechanism is offered to account for the pyridination of $Th^{\cdot+}$ and $PH^{\cdot+}$:

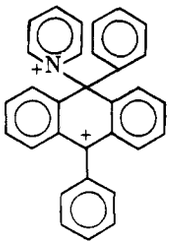


The attack of Py at the 3 position in this case is consistent with nucleophilic aromatic substitution under the direction of X^+.

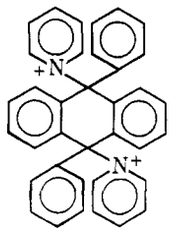
It is suggested that the 5-oxide is formed from hydrolysis of the dicationic $A(Py)^{2+}$ as follows:



The extent to which 5-oxide formation competes with pyridination is reflective of the relative reactivities of the $A(Py)^{2+}$ species. From the product distributions observed in acetonitrile, it is clear that $PH(Py)^{2+}$ is far less reactive than the corresponding $Th(Py)^{2+}$. The analogous intermediate in the case of the pyridination of $DPA^{\cdot+}$, $DPA(Py)^{2+}$, is also highly



$DPA(Py)^{2+}$



$DPA(Py)_2^{2+}$

reactive. This species, however, affords the dipyridinated ion[5], $DPA(Py)_2^{2+}$. Like $Th(Py)^{2+}$ and $PH(Py)^{2+}$, the pyridinium substituents in $DPA(Py)_2^{2+}$ are also labile,[5] but unlike the sulfur-containing species, reaction with protic nucleophiles (hydrolysis) does not kinetically favor the irreversible formation of the hydroxylated products.

Experimental Section

Materials. Acetonitrile (Burdick and Jackson Laboratories, UV grade) was purified as previously described.[27] Butyronitrile (Eastman) was purified in a similar manner. Py (J. T. Baker, reagent grade) was distilled from KOH at atmospheric ressure (bp 114–114.5 °C) and dried immediately prior to use by passage through activated alumina. Tetraethylammonium perchlorate (TEAP) was purified as reported elsewhere.[28] Phenothiazine (Aldrich) and iodobenzene (Aldrich) were used as received.

PH was prepared according to Gilman et al.[29] and purified by column chromatography (silica gel, CCl_4 eluent) followed by double recrystallization from glacial acetic acid (mp 94.5–95.5 °C, lit.[29] 94.5 °C). The perchlorate salt of the cation radical ($PH^{\cdot+}ClO_4^-$) was prepared in a manner analogous to that used by Shine et al.[3] for the synthesis of phenothiazine cation radical perchlorate. To a solution of 550 mg (2.00 mmol) of PH and 270 mg (1.06 mmol) of iodine in 40 ml of CH_2Cl_2 was added 3 ml of acetonitrile containing 420 mg (2.02 mmol) of $AgClO_4$. After stirring for 0.5 h, the AgI precipitate was filtered off and the filtrate added dropwise to 200 ml of anhydrous ether. The reddish-brown crystals formed were collected and dried in vacuo (25 °C) to yield 517 mg (1.38 mmol, 69%) of $PH^{\cdot+}ClO_4^-$, mp 250 °C dec. Anal. Calcd for $C_{18}H_{13}NSClO_4$: C, 57.68; H, 3.50; N, 3.74; S, 8.55; Cl, 9.46; O, 17.07. Found: C, 57.69; H, 3.48; N, 3.77; S, 8.57; Cl, 9.30; O, 17.19 (by difference).

PH(O) was prepared via oxidation of PH with hydrogen peroxide in refluxing EtOH[15] (mp 171–172 °C, lit. 172–173 °C).

Reaction of $PH^{\cdot+}$ ClO_4^- with Py. A solution of 590 mg (1.57 mmol) of $PH^{\cdot+}ClO_4^-$ in 40 ml of dry Py was stirred for 48 h. The solvent was removed and the resulting red solids dissolved in 200 ml of CH_3NO_2. This solution was repeatedly extracted with cyclohexane until TLC of the extract showed the absence of PH. The CH_3NO_2 fraction was evaporated to dryness, and the residue crushed and washed repeatedly with cold water to remove pyridinium perchlorate. The remaining orange crystals were dried in vacuo (25 °C), yielding 324 mg (0.72 mmol, 91% by eq 1) of *N*-[3-(10-phenylphenothiazinyl)]pyridinium perchlorate,[12] mp 110 °C dec, λ_{max} (acetonitrile) 255 nm (ϵ 3.22×10^4 M^{-1} cm^{-1}), 414 (3.10×10^3 M^{-1} cm^{-1}). Anal. Calcd for $C_{23}H_{17}N_2SClO_4$: C, 60.99; H, 3.78; N, 6.18; S, 7.08; Cl, 7.82; O, 14.13. Found: C, 61.18; H, 3.78; N, 6.18; S, 7.07; Cl, 7.58; O, 14.21 (by difference).

The cyclohexane extracts were combined and evaporated to yield 193 mg (0.701 mmol, 89% by eq 1) of PH. Removal of water from aqueous washings and subsequent recrystallization of the solids from aqueous MeOH gave 17 mg (0.652 mmol, 83% by eq 1) of pyridinium perchlorate, mp 286.5–288 °C (lit.[30] 287 °C).

The PH(O) formed when the reaction was carried out in acetonitrile/pyridine mixtures was isolated from the cyclohexane extracts by column chromatography (silica gel, CCl_4 and EtOH elution). Identification was by mixture melting point with authentic[15] material (171–173 °C) and comparison of UV spectra (EtOH).

Apparatus. Electrochemical measurements were carried out using

a conventional potentiostat[31] and cells described elsewhere.[4,5] Potentials are referred to the aqueous saturated calomel electrode. Working electrodes were fabricated from platinum foil (cyclic voltammetry) and platinum gauze (coulometry).

Spectra and kinetic transients were recorded on a Beckman Acta III spectrophotometer. The procedure employed for kinetic determinations consisted of pipetting 3.0 ml of Py or Py/acetonitrile solution into each of two matched cuvettes. The experiment was initiated by injection of a 10–20-μl volume of a stock $PH^{\cdot+}ClO_4^-$ solution (butyronitrile) into the sample cell, followed by rapid mixing. The molar absorptivity of $PH^{\cdot+}ClO_4^-$ in Py [8.32 ($\pm$.0.05) $\times 10^3$ M^{-1} cm^{-1}, 523 nm] was determined by extrapolation of the absorbance transient to zero time and comparison of the initial absorbance with that obtained from addition of an identical volume of the stock solution to 3.0 ml of butyronitrile [λ_{max} 515.5 nm, ϵ 8.70 ($\pm$0.07) $\times 10^3$ M^{-1} cm^{-1}]. All kinetic determinations were performed at 24.7 ($\pm$0.3) °C.

Registry No.—$PH^{\cdot+}ClO_4^-$, 52156-15-7; Py, 110-86-1; *N*-[3-(10-phenylphenothiazinyl)]pyridinium ClO_4^-, 61047-42-5; $PH^{\cdot+}$, 38130-02-8.

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(16) For an EE system involving two reversible couples

$$A \rightarrow A^{\cdot+} + e^- \quad (E_1)$$

$$A^{\cdot+} \rightarrow A^{2+} + e^- \quad (E_2)$$

the equilibrium constant for disproportionation, K_{dis}, may be calculated by[4]

$$2A^{\cdot+} \underset{}{\overset{K_{dis}}{\rightleftharpoons}} A^{2+} + A$$

$$K_{dis} = \exp\left(\frac{RT}{nF}|E_2 - E_1|\right)$$

From the data of Figure 1B, K_{dis} evaluates to be 2.2×10^{-12}.
(17) Calculated from the combined Stokes–Einstein and Smolunchousky equations:[18]

$$k_{diff} = \frac{8RT}{3000\eta}$$

For Py at 25 °, $\eta = 8.78 \times 10^{-3}$ P.[19]
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(21) The dielectric constant of neat Py is considerably lower[22] than that of even the most concentrated solution of Py in acetonitrile used in this work. This lower dielectric solvent stabilizes the transition state (see Conclusion section) more so than the reactants, thereby affording a higher reaction rate. A comprehensive examination of solvent effects on reactions of radical cations of EE systems is in progress.[23]
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Structure and Rearrangement of the Reduction Dimers of *N*-Alkyl Pyridinium Cations[1]

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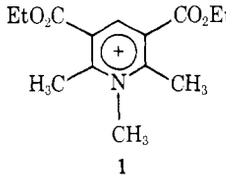
Reduction of the 1,2,6-trimethyl-3,5-dicarboethoxypyridinium cation (1) both chemically and electrochemically yields a mixture of isomeric reduction dimers. The less stable of these isomers, namely the 2,4′ dimer (8), undergoes rearrangement to yield the thermally more stable 4,4′ dimer **3** in a first-order reaction [$k = 1.1 \times 10^{12} \exp(-28.5/RT)$ s^{-1}]. A mechanism is proposed for the rearrangement that involves the thermal dissociation of the 2,4′ dimer 8 into two pyridinyl radicals (**5**) which recombine to yield the 4,4′ dimer **3**.

The reduction of the 1,2,6-trimethyl-3,5-dicarboethoxypyridinium cation **1** by sodium amalgam in aqueous acetic acid was reported by Mumm and his co-workers[2] to yield a dimeric reduction product that melted at 168 °C. Heating this material, which Mumm called "Primaester" ("primary ester"), resulted in its rearrangement to a higher melting isomer (mp 192 °C) referred to by Mumm as "Umwandlungester" ("transformation ester"). Mumm assigned the structure of the 2,2′ dimer **2** (1,1′,2,2′,6,6′-hexamethyl-3,3′,5,5′-tetracarboethoxy-1,1′,2,2′-tetrahydro-2,2′-bipyridine) to the "primary ester" and that of the 4,4′ dimer **3** (1,1′,2,2′,6,6′-hexamethyl-



1

$\xrightarrow[AcOH]{Na(Hg)}$ $C_{28}H_{40}N_2O_8$ "primary ester" mp 168 °C

$\xrightarrow{Heat}$ $C_{28}H_{40}N_2O_8$ "transformation ester" mp 192 °C (1)