VI. Degradation Reaction Kinetics of Polyaniline Studied by Rotating Ring-Disk Electrode Techniques

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ABSTRACT

The degradation reaction kinetics of oxidized polyaniline has been studied employing rotating ring-disk electrode techniques. Polyaniline films were grown on the disk electrode and were then oxidized at a potential more positive than 0.90V vs. Ag/AgCl, while the degradation product (benzoquinone) was monitored at the ring electrode at an applied potential of 0.05V. The product was monitored either with the disk potential maintained at >0.90V (closed-circuit experiment) or with the disk circuit disconnected after the polyaniline film was oxidized for some time (open-circuit experiment). The results of closed-circuit experiments indicate that electrochemical generation of oxidized polyaniline was a limiting step and its rate decayed for a given amount of polyaniline film according to the zeroth order. The rate of hydrolysis for the oxidized polyaniline in quinonoid forms was determined to be consecutive first order from open-circuit experiments. The dependencies of the hydrolysis reaction on the acidity of the degradation medium and sulfate concentrations have also been studied; the results are consistent with the Schiff base hydrolysis mechanism.

The use of polyaniline (PA) has been proposed in the areas of organic batteries (1-3), electrochromic displays (4), microelectronic devices (5), and corrosion inhibitors (6, 7). Unlike most other conductive polymers, PA is readily prepared in aqueous solutions by electrochemical or chemical oxidations, and the conducting form is stable in the air. In acid solutions, the resulting film structure is believed to be comprised mainly of repeating aniline units coupled together head-to-tail. Upon oxidation, the film becomes conductive, which, in acid or as a dry salt, seems to arise as a function of the extent of oxidation between the radical cation and the fully oxidized diimine form.

The proposed application of PA to some practical devices such as rechargeable batteries requires high stability of the material. Decays in the electrochemical responses for PA have been reported in several recent studies (4, 5, 8-11). In a study by Kobayashi et al. (9), they concluded that p-benzoquinone (BQ) is formed as a degradation product. We have also positively identified BQ as a degradation product of PA upon oxidation (12). In our current study, we report our results on detailed kinetic analysis of degradation products of PA using a Schiff base analogy is used to explain these dependencies. In addition, a consecutive first-order reaction mechanism is proposed that describes the role of differing surface groups on the observed decay curves.

EXPERIMENTAL

The RRDE work was carried out with a Pine RDE 3 bipotentiostat connected to a Pine ASR2 analytical rotator (Pine Instruments, Grove City, Pennsylvania). The electrode was Pine’s Model D76 RRDE with the manufacturer’s reported dimensions: disk radius, \( r_1 = 0.383 \) cm; ring inside radius, \( r_2 = 0.399 \) cm; ring outside radius, \( r_3 = 0.422 \) cm. This RRDE had a collection efficiency, defined as the ratio of ring to disk current, of 0.200 \( \pm \) 0.008 as determined by measuring the oxidation current for potassium ferricyanide at the disk and the reduction current at the ring for ferricyanide produced at the disk electrode. The bipotentiostat output was recorded with a Linseis LY1800 dual channel (X-Y) recorder (Linseis Recorder Company, Princeton Junction, New Jersey 08550). Steady-state outputs were also measured with a Keithley Model 181A multimeter.

REFERENCES

179 DMM. A Power Instruments C-891 RPM tachometer (Power Instruments, Skokie, Illinois 60076) was used to measure the rotation rate as well as to calibrate the rotation rate indicator on the Pine rotator.

The chemicals used were all reagent grade or better. The sulfuric acid (Ultrex, Baker) was used as received. The aniline (Eastman Organics) was used after distilling over zinc dust to eliminate the oxidized impurities. The clear aniline liquid was stored in the dark under an argon or nitrogen atmosphere. Hydroquinone (Eastman) was used after double recrystallization from water. All of the aqueous solutions were prepared with double distilled deionized water.

A 150 ml, capped, Pyrex container that was surrounded with a built-in water jacket, comprised the cell body. Holes of appropriate sizes were drilled through the cap. The solutions were deaerated with argon or nitrogen prior to use. The gases were passed through a purifier. The inert atmosphere blanketed the cell during the experiment. Constant temperature was maintained by pumping water from the water jacket through a Haake thermostated-water circulator set at 25.0° ± 0.2°C.

To maintain reproducible results, both the ring and disk electrodes were pretreated by potential pulsing between the cathodic and anodic limits such that H2 and O2 will be produced alternately. After each run, the PA remaining on the disk electrode was removed by immersion in a concentrated nitric acid solution.

**Results**

Closed-circuit experiments.—The studies reported here were all done in 1M H2SO4 as the supporting electrolyte for growth and for degradation. All of the PA films used for these experiments were grown in 0.055M aniline with the potential swept continuously between −0.1 to +1.2 V vs. Ag/AgCl (saturated KCl) at 50 mV·s−1 for a total of 10 cycles. This resulted in a film thickness of 0.45–0.55 μm, calculated from the charge-thickness relationship (11). The electrode was well rinsed with 1M H2SO4 to remove any soluble compounds left over from the growth solution.

First, we determined the potential at which the PA film began to degrade into soluble species. To do this, the disk potential was swept while the ring potential was held constant. The results are shown in Fig. 1. While the identical voltammograms were presented and discussed previously (12), we wish to address a few more points about the voltammograms here. Notice in the figure that the voltammograms at the disk electrode have peak shapes rather than mass-transfer-controlled limiting currents. This demonstrates that PA is, indeed, a surface species, even past the degradation potentials. At disk potentials more positive than 0.6-0.65V, a reducible compound is detected at the ring. This ring current shows significant hysteresis, indicating that the generation of the reducible compound may have some kinetic barrier. We believe that the hysteresis observed is in the time domain due to the delay in producing a product reducible at the ring electrode. That is, the electron transfer reactions at the disk are, most likely, followed by chemical reactions which produce the final soluble product seen at the ring electrode. When the disk potential was swept at lower rates (5 mV·s−1), the results were similar except that the reduction peak observed at most positive potential (∼0.7V) at the disk was no longer seen, due to the longer oxidation time and slower scan rate. The outcome of repeated cycling results in similar features on the disk electrode discussed earlier for the stability factor determinations (10). Based on our earlier results, the reducible compound detected at the ring is p-benzoquinone (12) or the immine. That is, some portion of the product could be benzoquinoneimine or diimine, which is hydrolyzed in solution to p-benzoquinone; the ring current would be equivalent in both cases.

Next, we ran chronoamperometric studies at the RRDE. In these experiments, the disk potential was pulsed from −0.1 to +1.2 vs. Ag/AgCl. The results in Fig. 2a show the disk current falling rapidly, while at the ring, there is a rise to a maximum followed by a slow decay. These features are better illustrated in Fig. 2b where these data were converted into the collecting efficiency. These data establish that at times of less than about 30s, the collection efficiency rises and, therefore, the overall hydrolysis reaction rate increases faster than the rate of generation of sites that can be hydrolyzed. Between 0.5 and 7 min the collection efficiency (Nc) is greater than 0.20 but it decreases monotonically. For any Nc > 0.20, the hydrolysis rate is greater than the rate of site generation, based on two-electron oxido-
dation at the disk resulting in one site formation. In this region, the collection efficiency for BQ generation decreases monotonically, following zeroth order. This observation leads to the following conclusion.

Initially, the rate of the chemical reaction, i.e., hydrolysis, to produce a reducible product detected at the ring electrode is slower than that of electrochemical generation of hydrolyzable sites. This explains not only the early rise in the ring current (<30s) but the hysteresis in Fig. 1. The hydrolysis reaction produces $\text{p-BQ}$ as a product as well as reduced PA with shorter chains through the termination step (12). The reduced PA thus produced is the source of a further anodic current. After some degradation reactions, the generation of reduced PA becomes a limiting step, and thus the disk current decreases. For times beyond 7 min $N_t < 0.2$, and there seems to be some trend toward a steady state. These circumstances suggest that the same fraction of the disk current goes toward side reactions that do not result in the formation of hydrolysis sites. A buildup in the number of sites is considered unlikely in view of the responses at shorter times. In the absence of side reactions, $N_t$ should become close to 0.2 and steady with time. It may be that steady state is achieved at some time past 7-10 min. We were unable to obtain reliable measurements for this time range due to the low currents and problems with baseline corrections. The uncertainty in the determination of $N_t$ increases with time since the currents decrease considerably. Between 7-10 min this uncertainty is about 10%.

Finally, we conducted an experiment to determine the relative amount of oxidizable soluble species that may be formed. The ring potential was set to +1.2V vs. Ag/AgCl. At this potential, compounds released at the disk, such as aniline or phenylenediamine (PDA), would be oxidized at the mass-transfer-controlled rates at the ring. The results (not shown) indicate that only a relatively small amount of oxidizable compounds comprise the soluble degradation products. The net signal is at most only between 3 and 6% of the reduction current observed at the ring under identical conditions at the disk. It can be concluded that only minor amounts of soluble species are in the reduced state and, as such, do not appear to be a major mechanistic path in the decomposition reaction of PA.

Open-circuit experiments.—The analysis of the hydrolysis rate can be considerably simplified if the PA-coated disk electrode is opened after the controlled potential oxidation at 1.2V, for example. Consider the following reaction sequence

$$
\begin{align*}
\text{(PA)}_n &\rightarrow (\text{PA})_n^+ + \text{BQ} & \text{(1)} \\
(\text{PA})_n^+ + \text{H}_2\text{O} &\rightarrow k_c (\text{PA})_{n-1}^+ + \text{BQ} & \text{(2)} \\
\text{d}(\text{BQ})/\text{d}t &= k_c (\text{PA})_{n-1}^+ & \text{(3)}
\end{align*}
$$

where $k_c$ is the overall electrochemical rate constant for the generation of hydrolysis sites, and $k_c$ is the overall rate for the chemical reactions that lead to hydrolysis of sites. Upon open circuit, the rate of formation of these sites is zero and then the ring current becomes a measure of the chemical oxidation rate (S); for example, if the overall decay follows first-order kinetics

$$
\text{S + H}_2\text{O} \rightarrow k (\text{BQ} + \text{D})
$$

the rate of BQ generation, measured by the current at the ring, should decay exponentially if it follows the first-order kinetics. Thus, the $\ln(1/t_D)$ vs. $t$ plot would be linear for the first-order decay. In some other reactions of a second-order kinetics, the $\ln(t_D)$ vs. $t$ plot would be linear, indicating a second-order kinetics. For the PA-coated electrodes, the log plots were linear or curved, depending on pH. Due to this curvature, we believe that the actual reaction kinetics is consecutive first order, complicated by hydrolysis termination steps. For consecutive first-order reactions, a mixed exponential decay is realized which results in $\ln(t_D)$ plots that may be linear or curved, depending on the values for the rate constants. Under conditions where curvature was observed, the data was split into two linear regions, the slopes of which have been denoted as $k_1$ and $k_2$.

An example of the comparative effects of open-circuiting the disk is shown in Fig. 3 where the closed- and open-circuit curves are plotted together. Note that when the disk is open-circuited the ring current decays to background within 200s, while in the closed-circuit situation there is still a considerable ring current after 200s. Repeating this procedure on the same film indicated that the film decomposition is not complete after the first cycle. This is consistent with our previous observations (12) where the open-circuit decay was shown to be incomplete, and again, it can be concluded that there are some termination steps in the open-circuit mechanism.

In addition, the open-circuit decay became slower with each successive cycle. Decay constant, $k_c$, fell from 0.030 s$^{-1}$ for the first cycle to 0.025 for the third. Moreover, the time for the disk to reach a closed-circuit maximum increased. Both of these behaviors are not consistent with what was observed for films as a function of thickness. It is shown below that thinner films exhibit apparent faster decay as well as shorter times to reach closed-circuit maximum and smaller current values. These observations are consistent with the compositional changes in the PA structure with hydrolysis time. As observed previously (11), films that had been subjected to continuous cycling were no longer soluble in DMF after conversion to the base form.

Clearly, to compare the results for different films, reproducible results can only be obtained with reference to a particular cycle number. As such, all the data presented in this paper are for the first cycle only.

The acidity, total sulfate, and thickness dependencies. The function of the acidity on the observed current was determined in HCl and H$_2$SO$_4$. Sodium sulfate (Na$_2$SO$_4$) was added to the sulfuric acid solutions to maintain the total sulfate concentration at 2M. This results in a constant ionic strength of about 2 for pH below 1 or so. Above this pH value the ionic strength rises, but we found that there was little effect compared with the total sulfate concentration (see the following and Table I). Adjusting the ionic strength to 6 was impractical. The pH of these mixtures was calculated using $pK_{as} = 1.98$ for the monohydrange sulfonate anion (14). For studies in HCl, NaCl was added to solutions of HCl concentrations less than 1M. At least two, for the most part three, and sometimes four or five determinations of the experimental decay curves were obtained for each solution at a particular pH. For studies in sulfuric acid, the disk potential was stepped from -0.1V to either 0.9 or 1.2V. In HCl the disk potential was stepped to only 0.9V to avoid Cl$^-$ oxidation. The PA film growth procedures were the same as described in the closed-circuit experiments, except for the pH studies where the electrode was rinsed in the electrolyte used for degradation and for the thickness studies where the number of cycles for growth varied.
Table I. Hydrolysis rate data for other growth and degradation conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>Growth conditions</th>
<th>Degradation conditions</th>
<th>$k_1$ (s$^{-1}$)</th>
<th>$k_2$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.1+1.2V</td>
<td>0.5M HSO$_4^-$</td>
<td>0.009</td>
<td>0.021</td>
</tr>
<tr>
<td>2</td>
<td>1M NaHSO$_4$</td>
<td>1.5M Na$_2$SO$_4$</td>
<td>0.012</td>
<td>0.019</td>
</tr>
<tr>
<td>3</td>
<td>1M NaHSO$_4$</td>
<td>1.0M H$_2$SO$_4$</td>
<td>0.043</td>
<td>0.020</td>
</tr>
<tr>
<td>4</td>
<td>-0.1-0.9V</td>
<td>0.5M Na$_2$SO$_4$</td>
<td>0.045</td>
<td>0.025</td>
</tr>
<tr>
<td>5</td>
<td>1.0M H$_2$SO$_4$</td>
<td>1M NaHSO$_4$</td>
<td>0.019</td>
<td>0.025</td>
</tr>
<tr>
<td>6</td>
<td>-0.1-1.2V</td>
<td>1.0M NaHSO$_4$</td>
<td>0.014</td>
<td>0.016</td>
</tr>
<tr>
<td>7</td>
<td>1.0M H$_2$SO$_4$</td>
<td>0.9V</td>
<td>0.014</td>
<td>0.016</td>
</tr>
<tr>
<td>8</td>
<td>-0.1-1.2V</td>
<td>1.0M H$_2$SO$_4$</td>
<td>0.028</td>
<td>0.016</td>
</tr>
<tr>
<td>9</td>
<td>0.5M Na$_2$SO$_4$</td>
<td>0.9V</td>
<td>0.0275</td>
<td>0.017</td>
</tr>
</tbody>
</table>

*Scan rate = 50 mV/s. Aniline concentration = 0.055M. All the films were grown to an initial thickness of ~0.5 μm.

The open-circuit decay and the closed-circuit ring currents increase with acidity, while the time to reach the closed-circuit ring current maximum decreases with acidity. Shown in Fig. 4 are some of the open-circuit decay curves and the log plots for these data. Note that in 1.5M H$_2$SO$_4$ + 0.5M Na$_2$SO$_4$ solutions there is a definite curvature in the log plot. The curvature in the semilog plots of the normalized open-circuit ring current decay always increased with acidity. In cases where two lines are observed in these plots as in Fig. 4c, two rate constants $k_1$ and $k_2$ were obtained from shorter and longer time domains, respectively. In no case was this curvature seen at higher pH; the break was between 0.5 and 1.0M acid. Control experiments established that this curvature was not due to a buildup of BQ in solution.

The curvature effect does not arise from a change in the $i/E$ behavior of BQ at higher acidities. Control studies on BQ reduction over the range of acidities used in this study, and at a constant BQ concentration, resulted in ring steady-state currents which did not vary significantly. The disk current was at open circuit for these control studies. It should be pointed out that at pH ≥ 4 the current would change, as n changes from 2 to 1 due to high stability of BQ anion radicals, complicating the interpretation of results and, without extensive controls, rendering them unreliable.

Shown in Fig. 5 are the values obtained for $k_1$ and $k_2$ as a function of the H$^+$ concentration. As can be seen, a plateau in $k_1$, and $k_2$ is about the only common feature seen in these two acids. The limiting value is slightly higher in HCl than H$_2$SO$_4$. The observed decay rates are considerably greater in sulfuric acid solutions when the H$^+$ concentration is less than about 1M.

Fig. 4. Ring current and log of ring current vs. time. Current at t = 0 is i(0). The growth and other conditions as in Fig. 3 except (a) in 0.5M H$_2$SO$_4$ + 1.5M Na$_2$SO$_4$, (b) 1.0M H$_2$SO$_4$ + 1.0M Na$_2$SO$_4$ and (c) 1.5M H$_2$SO$_4$ + 0.5M Na$_2$SO$_4$.

Fig. 5. Rate constants, $k_1$ and $k_2$ vs. [H$^+$]. (a) Results in HCl solutions. (b) Results in H$_2$SO$_4$. 

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Fig. 6. Average $k_1$ values vs. pH or $H_0$: (a) in HCl, and (b) in $H_2SO_4$.

Employed. This function ($H_0$) is a comparative measure of the solvent to donate protons to weak base molecules and is commonly used to replace pH values in solutions of high acidity (14-18). The $H_0$ values, which include corrections due to the salt effect, were taken from the data and tables given by Paul and Long (14). The salt effect correction term for $NaClO_4$ was used for $NaHSO_4$ as the sulfate data were not available. The values can be expected to be close to each other because the salt effects are more sensitive to changes in the cation. Employing these $H_0$ values in place of pH tends to broaden the curve and shift it toward higher acidity, but the shape remains the same. The $H_0$ values are retained in further analysis since they are a more reliable indicator of the true acid strength.

Between pH (or $H_0$) 0-3, the rate constant is notably higher in sulfuric acid. This observation is consistent with the stability factors reported previously (10, 12) and prompted us to study the effect of the sulfate concentration at constant pH. The results for pH = 1, Fig. 7, shows that $k_1$ observed as well as the closed-circuit maximum ring current increases linearly with the total sulfate concentration. Evidently, the sulfate acts as a catalyst in the hydrolysis reaction. The ionic strength was maintained at 2 with $NaCl$. Under more acidic conditions, the plots were all linear. The catalytic effect, indicated by slopes of plots (not shown) decreased somewhat as the acidity of the medium increased, implying that both $HSO_4^-$ and $SO_4^{2-}$ species act as catalysts.

Finally, the variations in $k_1$ and $k_2$ with film thickness, in 1M sulfuric acid, are shown in Fig. 8. The $k_1$ values seem to follow a $-1/2$ power dependency on film thickness. For the $k_2$ values there is a definite downward trend with thickness (not shown). Indeed, for thicknesses above 1 μm, the semilog plots were linear and so there was no $k_2$. The decrease in the $k_2$ values may follow a linear or $-1/2$ power dependency with thickness, but the scatter in $k_2$ values precludes any firm assignment to the function.

The change in the hydrolysis rate with thickness might be associated with the diffusion of the reactant ($H_2O$) through the film. The thickness effect may be explained by structural differences between thin and thick films. These points are discussed in more detail below.

The maximum closed-circuit ring current showed an increase with thickness, although there was considerable scatter (not shown). As expected, comparatively thinner films took less time to reach the maximum current as the amount of material is less and is used more quickly.

Miscellaneous rate data.—The results for other growth and degradation conditions that were studied are summarized in Table I. Comparison of entries 1-3 to the rate data in Fig. 5b shows that films grown in 1M NaHSO$_4$ are somewhat more stable than those grown in 1M $H_2SO_4$. Comparing entry 4 to entry 5 shows that films grown to a switching potential of 0.9V are less stable than those that are
switched at 1.2V. Both of these findings are consistent with the stability factors reported previously (12). By comparing entry 5 to 6 and 7 to 8, it can be seen that there is little difference in the observed decay between films open-circuited from 0.9 or 1.2V. These data are consistent with the cyclic voltammetric results discussed previously (11, 12); the more positive oxidation wave, peaking between 0.75-0.85V, was assigned to the conversion of PA into the fully oxidized form. The effect of ionic strength was found to be quite minimal, as shown by comparison of entry 9 to entry 10.

The results between films were very reproducible. The minimum decay rate that could be measured was between 0.003 and 0.005 s⁻¹. For decay rates below this, the ring current was not sufficient to reliably separate the signal from the noise and from the background. As shown above, the scatter in the results is about equal to the minimum detection limit.

Discussion

Any proposed mechanism for the hydrolysis of polyaniline should account for the observed behaviors as much as possible. These include the following: (i) the acidity effect, (ii) the sulfate effect, (iii) the curvature in the In (ln) vs. time plots, and (iv) the thickness effect. In the first part of our discussion, the acid and sulfate effects are discussed. The second part deals with the curvature while the thickness effect is covered in the last section.

The acidity and sulfate effects—PA hydrolysis modeled as a Schiff base.—In the broadest sense, a Schiff base is any molecule with an azomethine group [R=N=N-R(H)]. More frequently, though, the term Schiff base refers to an acyclic imine derived from an aliphatic or aromatic amine. The hydrolysis reaction of the imine group requires at least two steps. Depending on pH, either the formation or the decomposition of the carbinolamine intermediate (or the zwitterion equivalent) is the rate-determining step; this reaction is, in most cases, reversible. Numerous review articles and monographs are available on the formation and hydrolysis of Schiff bases (16, 19, 20).

For the hydrolysis of Schiff bases derived from most aliphatic amines, a bell-shaped curve results when the observed rate constant is plotted vs. pH. This feature is thought to arise from a change in the rate-determining step near the pKᵢ for that base which inhibits the formation of the zwitterion at low pH (16, 19, 20). In the case of Schiff bases derived from weakly basic amines, the bell-shaped curve is either shifted to lower pH regions or, in many cases, a maximum rather than a point of inflection is observed (16, 19-22). In strong acid, if an inflection point is finally observed, this decrease in the rate is attributed to a decrease in the activity of water rather than to a change in rate-determining step (19, 20, 22). The water acts as a nucleophilic agent or as proton acceptor during the decomposition step of the intermediate carbinolamine.

The dependence of the observed hydrolysis rate for PA as a function of acidity is consistent with previous results reported for the hydrolysis of weakly basic amines. The shape of the experimental curve for kᵢ observed in HCl was quite similar to the results published by Reeves (21) for the hydrolysis of benzylideneaniline as a function of acidity. Reeves proposed a hydrolysis mechanism to explain the observed behavior, which was actually a more general case of one first suggested by Willi and Robertson (29). We have adopted this mechanism to account for our results on PA. To this reaction scheme we have added steps to account for the sulfate effect; our scheme is shown in Fig. 9. Steps 7 and 8 were added to account for the sulfate effect, but otherwise this is the same mechanism as used by Reeves (21).

Steps 1-6 are depicted in Fig. 10 for the general case. The dependence of the observed hydrolysis rate for PA as a function of acidity is consistent with previous results reported for the hydrolysis of weakly basic amines. The shape of the experimental curve for kᵢ observed in HCl was quite similar to the results published by Reeves (21) for the hydrolysis of benzylideneaniline as a function of acidity. Reeves proposed a hydrolysis mechanism to explain the observed behavior, which was actually a more general case of one first suggested by Willi and Robertson (29). We have adopted this mechanism to account for our results on PA. To this reaction scheme we have added steps to account for the sulfate effect; our scheme is shown in Fig. 9. Steps 7 and 8 were added to account for the sulfate effect, but otherwise this is the same mechanism as used by Reeves (21). Steps 1-6 are depicted in Fig. 10 for the general case. The simple model (16, 19, 20) represented by steps 1, 3, and 5 (k₋₂ = 0), predicts that the rate of BQ production is proportional to the fraction of Schiff base that is in the protonated form (rate = Cᵢ[SH⁺]/[S + SH⁺]). When k₋₂ ≠ 0, the rate decreases at low pH, depending on k₋₂. Reaction schemes using this step are employed when a bell shape in the rate vs. acidity plots is observed. For weakly basic aromatic amines, steps 4 and 6 are invoked in order to explain the observed lack of an inflection point at low pH (21-22). These steps involve the formation and subsequent parallel decomposition path of the protonated carbinolamine intermediate, and are considered reasonable because the electron withdrawing phenyl group permits amine expulsion with less driving force than aliphatic amines (20).

Three reaction schemes which would account for the observed sulfate effect are shown in Fig. 11. General base catalysis by the sulfate anion to form the intermediate is represented by step 7 in the hydrolysis scheme. We have not included the activity effect due to the lack of the effect of ionic strength as already pointed out. Also, measurements were made at constant ionic strengths. Several

![Fig. 9. Hydrolysis mechanism for PA—the pH effect](image)

![Fig. 10. Hydrolysis schemes for weakly basic amines](image)
mechanisms are possible, all of which lead to different transition states but result in the same product (19a). For the catalysis scheme shown in Fig. 11a, the proton is donated by a water molecule. Swain et al. (23) have argued in favor of an alternative transition state where a proton is abstracted at the nitrogen. In Fig. 11b the possibility of a general base catalysis of the protonated intermediate is shown. This path can be considered unlikely since an inspection point was not observed (see Ref. 19a, pp. 479 and 493).

Whatever the mechanism, an increase in rate at constant pH by phosphate, acetate, and other conjugate bases has been routinely observed in a variety of Schiff base hydrolysis reactions (19-29). In view of this, our data showing a rate enhancement by sulfate at pH = 1 should come as no surprise. To explain product distributions in the hydrolysis of iminolactone derivatives with pH, Cunningham and Schmir (28) have proposed a catalytic process whereby the protonated form of the buffer is involved, via a concerted cyclic proton shift with the neutral carbamolamine intermediate. An analogous process when applied to HSO₄⁻ is covered by step 8 in the hydrolysis scheme and is depicted in Fig. 11c.

The net outcome of such a reaction would be to shift the equilibrium between the uncharged carbamolamine toward the zwitterionic form. As mentioned earlier, a decrease in the concentration of the zwitterion leads to a decrease in rate. It follows that any reversal of this process would result in an apparent increase in the observed rate. A concerted proton transfer mechanism has also been proposed by Willi and Robertson (29). This scheme also predicts that a relative decrease in the concerted proton shift pathway would occur at even higher acidities because the intermediate exists mainly in the protonated form. The data establish that this trend is realized. In 2M H₂SO₄, the observed rate is, in fact, slightly lower than the rate in 2M HCl.

The rate equations (Fig. 9) may be solved to express kₐₙ₉ as a function of [H⁺] (see Appendix). If [HSO₄⁻] = [SO₄²⁻] = 0, the solution is equal to the one given by Reeves and may be expressed in the form

\[ k_{\text{obs}} = \frac{A + B[H^+] + C[H^+]^2}{D + E[H^+] + F[H^+]^2} \]  \[ \text{(5)} \]

When the [H⁺] is high, only the quadratic terms are important and the rate equals C/F. At low [H⁺] the rate reduces to the A/D terms. At intermediate pH, the B/H⁺/D or C[H⁺]/E[H⁺] terms follow the linear region. The parameters chosen for the fit were based on ratios determined for the limiting cases. It should be pointed out that these ratios are not absolute values, and, therefore, it is not possible to evaluate any of the individual rate constants (19a, 21).

When the additional terms are added to reflect the behavior in sulfuric acid, Eq. [5] may be expressed as

\[ k_{\text{obs}} = \frac{A + (B + B'[SO₄²⁻]) + B'[HSO₄⁻][H⁺] + (C + C'[SO₄²⁻]) + C'[SO₄²⁻][H⁺][H⁺]}{(D + D'[HSO₄⁻]) + (E + E'[HSO₄⁻])[H⁺] + F[H^+]^2} \]  \[ \text{(6)} \]

A fit of Eq. [5] with the results obtained in HCl is shown in Fig. 12. Also shown in this figure are curves resulting from the simple model, assuming Kₐ₌ = 1.62 or 0.1. This model considers only steps 1, 3, and 5 in Fig. 9 (k₃ = 0), and has the rate expression

\[ \text{rate} = C \frac{[SH^+]}{[SH⁺]} \]

The actual value for Kₐ₃ is unknown. MacDiarmid et al. (2, 30) found that the chloride content determined for dry palladium chloride salts (oxidized probably an oxidized form) decreased considerably when washed in pH = 3 (HCl) solutions compared to pH = 1 solutions; this implies that Kₐ₃ lies somewhere within this range. DeSurville et al. (1) observed two breaks in the titration curve of PA sulfate with NaOH. Orata and Buttry (31) estimated the pKa value of PA at -0.3 to -0.4 and >1 for reduced and oxidized forms, respectively. From these, a value of Kₐ₃ = 0.1 seems reasonable for the sulfate form. A Kₐ₃ of 1.62 is improbable because the salt form is readily isolated from solutions containing as little as 0.1M acid. A more likely explanation is that the rising portion of the curve more closely follows k₄ (Fig. 9), the protonation of the intermediate, and that the decomposition of this form is the rate limiting step at these acidities. In conclusion, these data were found to be consistent with the hydrolysis mechanism outlined in Fig. 9. Furthermore, the fit from the more complex relationship is superior to the fit from the simple model, irrespective of the value chosen for Kₐ₃.

In Fig. 13, the curve derived from Eq. [6] is compared with the results obtained in sulfuric acid. Also shown is the curve that results if the sulfate terms are neglected (Eq. [5]). Clearly, the curve where the sulfate terms are included gives a much better fit with the observed behavior. We wish to point out that a very similar fit for pH > 1 was obtained when just the catalysis by SO₄²⁻ is considered (k₄ = k₅ = 0). Under these conditions, the rapidly rising portion of the curve is shifted toward a somewhat higher acidity, but still well within the range indicated by scatter of the measurements. It was found necessary, however, to neglect the C' term (C' = k₄/k₅) in order to avoid an over-

\[ B + H_2O \rightarrow A + H_2O \rightarrow BQ \ (QI) \]

\[ A \rightarrow P \]

\[ B \rightarrow P \]

The overall termination steps \[8\]-\[9\] represent the overall rate for processes which consume quinonoid sites by pathways other than hydrolysis into BQ or QI.

The rate equations for these processes are

\[ \frac{d[B]}{dt} = -[B](k_2 + k_{75}) \]

\[ \frac{d[A]}{dt} = -[A](k_1 + k_{77}) + k_2[B] \]

\[ \frac{d[BQ]}{dt} = k_2[A] \]

It is now assumed that \( k_{71} \ll k_1 \) and \( k_{75} \ll k_2 \). By employing this approach, the values for \( k_1 \) and \( k_2 \) will tend to be inflated from the true value. It is recognized that the validity of this assumption may be questioned; nonetheless, this is the only practical method which yields any insights into the hydrolysis mechanism. Accepting this, Eq. \[11\] may be solved for \( A \) as a function of \( t \)

\[ A = \frac{k_2[B][exp(-k_2t) - exp(-k_1t)]}{k_1 - k_2} + [A_0] exp(-k_1t) \]

Realizing that \( d[BQ]/dt = k_2[A] = i \) and thus \( k_2[A] = i_o \), we obtain an expression

\[ i = \frac{k_2[B][exp(-k_2t) - exp(-k_1t)]}{[A_0] (k_1 - k_2)} + k_2[A] \]

where \([A]_0 = [A] \) at \( t = 0 \), and \([B]_0 = [B] \) at \( t = 0 \). The last term on the right accounts for the fact that \([A]_0 = 0 \) at \( t = 0 \). Assuming an octamer model for PA, the \([B][A]_0 \) ratio is not greater than 6 (there are two sites on each chain group).

The solution sets for the case \( k_1 = k_2 \) (not shown) did not follow the observed results. The curvature was convex and, in most instances, there was a considerable induction time \((i_o/2 \pm 0.5 \ t \ \text{flat})\). The case \( k_2 > k_1 \) was also tried and dismissed. Again, the curvature was going the wrong way and, in many cases, there was a rise in the current after open circuit. This situation was considered unlikely. If \( k_2 \) was much greater than \( k_1 \), comparatively large amounts of oxidizable material would be expected at the ring. This was not seen, as was discussed earlier.

The case where \( k_1 > k_2 \) provides a good fit with the observed behavior. In Fig. 15 a set of data points obtained in 1.5M HCl are plotted along with the resulting curves where \( k_1, k_2 \), and \([B][A]_0 \) were changed systematically. As can be seen, the fit to the data points is quite sensitive to a change in any of the parameters. The effects induced by \( k_1 \) are quite unlike the more familiar situation where \([A]_0 = 0 \) at \( t = 0 \) (16). The fast decay term is still retained because Eq. \[14\] reduces to an exponential sum when \( k_1 > k_2 \). A fit over the entire acidity range in HCl is given in Fig. 16. There is good agreement between the data points and the theoretical curve. It can be concluded, therefore, that the results are consistent with a consecutive reaction mechanism. The values from the simulated curves are higher than the experimental values taken from the slopes. A comparison for the data shown in Fig. 16 is listed in Table II.

A major difficulty that precludes any absolute comparisons of the PA hydrolysis data with the theoretical values obtained from the curves shown above lies in our lack of knowledge of the actual \([B][A]_0 \) ratio. The values for \( k_1 \) and \( k_2 \) obtained from the simulated curves are strongly dependent on the \([B][A]_0 \) ratio. For an equivalent fit to the

\[ \text{Fig. 13. Comparison of experimental points (E) to simulated curves for PA hydrolysis in } H_2SO_4: (a) neglecting sulfate terms in Eq. \[6\] and using } A = 0.1, B = 0.45, C = 0.36, D = 0.45, E = 1.32, and } F = 6.75; (b) including sulfate terms, } A-F \text{ the same as in } a, B' = 30, B" = 0.2, C' = 9, C" = 9, D' = 2, and } E' = 6. \]

\[ \text{Fig. 14. A consecutive reaction scheme for PA hydrolysis} \]
data, an increase in the ratio causes an increase in \( k_1 \) and \( k_2 \). In this respect, the values obtained from the simulated curve are somewhat arbitrary. The \([B]/[A]_o\) ratio for the octamer is 6/1. When one chain group is hydrolyzed the ratio drops to 4/1, and so on. Recall that the circuit could not be opened until some hydrolysis had occurred. As mentioned above, the \( k_1 \) and \( k_2 \) values derived from the simulated curves are quite sensitive to any changes in \([B]/[A]_o\) ratio. When fitting the data taken from 1.5M HCl, and using \([B]/[A]_o = 2.1\), \( k_1/k_2 = 6.5\), but by using \([B]/[A]_o = 3\), and for an equivalent fit \( k_1/k_2 \) must rise to 12.

To a first approximation, one would expect no difference between \( k_1 \) and \( k_2 \) as both sites are adjacent to a phenyl group. This discrepancy observed in our study may be due to steric hindrance effects on the internal chain groups. The three-dimensional structure of the film is more rigid in the oxidized form due to the change in geometry from tetrahedral to planar caused by formation of the carbon nitrogen double bond. It is expected that the internal chain groups would behave more as an insoluble solid salt ionically bonded with the counterion. On the other hand, the tail groups are in direct contact with solution. The first step in the hydrolysis reaction requires a perpendicular approach by the nucleophile (20).

Constraints in the experimental procedures may also account for some of the hindrance effects. Upon oxidation of the film, there is some time during which a fair number of internal chain groups, which are in the closest proximity with the solution, could be hydrolyzed to end groups because the circuit is opened; thus, at open circuit only those sites that are relatively hindered may be measured. This is consistent with the fact that the observed rate constant decreases with cycle number.

An underlying assumption of the consecutive reaction mechanism is that there is little or no difference in the hydrolysis rate between quinonediimine and quinoneimine end groups. There is a solid basis for making this assumption. Adam's group (37) could detect no difference in the observed rate of hydrolysis between phenylenediamine (PDA) and p-aminophenol (PAP) to benzoquinone at acidities where both the nitrogen groups on PDA were protonated. Tong (38) found that the rate of hydrolysis of quinonediimine to quinoneimine was double the hydrolysis rate of quinoneimine to benzoquinone in alkaline solutions. This is to be expected in that there are two nitrogens in quinoneimine. At intermediate pH ranges, \( k_1 \) was 6-10 times greater than \( k_2 \) for hydrolysis of quinoneimine.

This was attributed to the differences in the pK\(_a\)'s on the nitrogen groups (pK\(_{a1} = 2\), pK\(_{a2} = 6\)). Thus, if the curvature was due to a difference in the hydrolysis rate between quinonediimine and quinoneimine end groups, it would be noted in the data with increasing pH. This is quite the opposite of what was observed and leads us to conclude that the hydrolysis rates of these two end groups are indistinguishable.

The range of values which was assigned to reflect hydrolysis of the end groups, \( k_1 \), compares reasonably well for the analogous solutions species. Leedy and Adams (39) determined that \( k = 0.029 \text{s}^{-1} \) for the hydrolysis reaction of the oxidized form of N-phenyl-p-aminophenol in 1M HClO\(_4\). For solubility reasons they used a solution that was 50% acetone. Determinations at pH 0.5 and 1 resulted in \( k = 0.037 \) and \( k = 0.010 \text{s}^{-1}\), respectively. For acidities \( H_2O \leq 0\), our values for PA differ considerably from the ones taken from Adams (37) where \( k \) falls from 0.029 \text{s}^{-1} \) to \( -0.002\), from \( H_2O = 0 \) to \( H_2O = 1\). The bell shape they observed could be due to the solvent effects and the lower concentration of water used in their studies (18, 21), but otherwise this discrepancy remains unclear.

**The thickness effect.**—The decrease in the observed hydrolysis rate with increasing thickness may be due to structural changes. In our earlier study (40), the film growth was shown to be proportional to (thickness)\(^{-1/2}\); this was explained in terms of a reaction zone or penetration depth into the film. This same effect may also apply to PA hydrolysis reactions. Carlin et al. (41) noted a transition from a relatively dense polymeric structure to one of loosely packed fiber-like structures with film thickness. This phenomenon could open channels in the film structure, thereby increasing the accessibility of the solution to internal chain groups. Such a model predicts an increase in the \([B]/[A]_o\) ratio with thickness. In Fig. 15c it was shown that an increase in the \([B]/[A]_o\) ratio, at constant \( k_1 \) and \( k_2 \), will decrease the measured or observed rate constants. We see that the thickness data fits this model, and therefore it can be concluded that an increase in the \([B]/[A]_o\) ratio with thickness is consistent with the observed behavior.

An alternative approach is to assume that the observed ring current follows the diffusion of the BQ product through the film or the diffusion of the reactant (H\(_2\)O) into the film from the solution/film interface for the normalized ring current with time (42)

\[
\frac{1}{k_1} = 0.5 \exp(-At) + \exp(-9At) \quad [15]
\]

where \( A = D\pi^2/4h^2 \), \( h \) = film thickness, and \( D \) = the diffusion coefficient for BQ through the film.
Upon analysis, however, Eq. [15] does not fit the observed behavior. At longer times (>40s) the second term is negligible, and $A = k_2$. From this, an approximate value for $D = 3 \times 10^{-13}$ cm$^2$/s, was obtained from the slope of $k_2$ vs. (thickness)$^2$. With $D$ in hand, curves of Eq. [15] were obtained for the thickness range of 0.3-1.0 $\mu$m. From these curves, the measured slopes in the initial fast decay ($k_1$) ranged from 0.0035 to 0.035 s$^{-1}$. This range was much larger than the observed range of 0.02-0.035 s$^{-1}$. We therefore conclude that diffusion of product is not a limiting step. This conclusion is consistent with the pH and sulfate effects. If product diffusion was the limiting step, then it can be expected that these other functionalities would not be manifest. Moreover, Oyama et al. [43] have shown that larger molecules, such as ferro/ferricyanide, are not permeable into PA films. On the other hand, it may be that product or reactant diffusion exerts a less than limiting effect on the results. It was not possible to evaluate intermediate cases.

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APPENDIX

The derivation of the expression for the observed rate as a function of the $[H^+]$ is based on the rate equations given in Fig. 14. With the exception of the added sulfate terms, this derivation closely follows the work by Reeves (21).

First, the equilibrium and related expressions are listed

\[ S + SH^- = S_T \]  
\[ K_{SH^+} = \frac{[H^+][S]}{[SH^+]} \]  
\[ K_a = \frac{[SO_4^{2-}][H^+]}{[HSO_4^-]} \]  
\[ K_r = \frac{[SHO_2H^+]}{[SHOH][H^+]} \]

By combining [A.1] and [A.2]

\[ [SH^-] = S_T \left( \frac{[H^+]}{[H^+]} + K_{SH^+} \right) \]  
[A.5]

The rate of disappearance of hydrolysis sites into products is

\[ -\frac{dS_T}{dt} = k_6[SHOH] + k_6[SHOH][HSO_4^-] \]  
[A.6]

or, by use of [A.4]

\[ -\frac{dS_T}{dt} = [SHOH]k_5 + K_6k_6[H^+] + k_6[HSO_4^-] \]  
[A.7]

Now, the rate of formation of SHOH is

\[ \frac{d[SHOH]}{dt} = k_4[S] - k_4[SHOH] + k_4[SH^+] - k_4[SHOH][H^+] \]

Using the steady-state approximation, $d[SHOH]/dt = 0$, we obtain

\[ [SHOH] = \frac{k_4[S] + k_4[SH^+] + k_4[SHO_2H^+]}{(k_2 + k_5) + (k_3 + K_6k_8 + k_8k_6)} \]  
[A.9]

The rate in terms of $[SH^-]$ can now be obtained by combining [A.9] with [A.7], and after some algebra and utilizing [A.2]-[A.4], we obtain

\[ -\frac{dS_T}{dt} = [SH^-] \left( \frac{k_2k_6k_8 + k_3k_6 + k_8k_6k_9}{(k_2 + k_5) + (k_3 + K_6k_8 + k_8k_6)} \right) \]

or, to shorten the expression

\[ -\frac{dS_T}{dt} = [SH^-](a + b) \]  
[A.11]

Now the forward rate is

\[ -\frac{dS_T}{dt} = \frac{dQ}{dt} = k_r ([S] + [SH^+]) = k_r [S_T] \]  
[A.12]

and, from [A.11] and [A.5]

\[ -\frac{dS_T}{dt} = [SH^+](a + b) = [S_T] \left( \frac{[H^+]}{[H^+] + K_{SH^+}} \right) (a + b) = k_r [S_T] \]  
[A.13]

Therefore, the observed forward rate is

\[ k_f = \left( \frac{[H^+]}{[H^+] + K_{SH^+}} \right) (a + b) \]  
[A.14]

After multiplication and collection of terms

\[ k_f = A + B'[SO_4^2-] + B''[HSO_4^-][H^+] + C + C'[SO_4^2-] + C'[SO_4^2-][H^+] \]

\[ D + D'[HSO_4^-] + D' + E'[HSO_4^-][H^+] + F[H^+] \]

[A.15]

where

\[ A = k_6k_8K_{SH^+} \]
\[ B = k_6k_9 + K_6k_8 + k_8k_6 \]
\[ B' = k_6k_7 \]
\[ C = k_6k_8 \]
\[ C' = k_6k_9 \]
\[ C'' = k_6k_6 \]
\[ D = k_{SH^+} + (k_2 + k_5) \]
\[ D' = k_{SH^+} + (k_3 + k_6) \]
\[ E = k_{SH^+} + (k_3 + k_6k_8(k_2 + k_5)) \]
\[ E' = k_{SH^+} + k_6 \]
\[ F = k_{SH^+} + k_8k_6 \]

When the sulfate concentration is zero, Eq. [A.15] reduces to the equivalent expression published by Reeves (21).

REFERENCES

Conductivity and Anisotropy of Electrochemically Prepared Conducting Polypyrrole Films

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ABSTRACT

Thick, freestanding, flexible films of polypyrrole have been prepared from pyrrole monomer in propylene carbonate solvent containing tetra ethyl ammonium p-toluene sulfonate electrolyte. Films were electrodeposited onto titanium substrates at temperatures from -40°C to 25°C, and were found not only to have high conductivity, but were also anisotropic. The electrodeposition temperature, electrode dimensions, current density, voltage, and solvent were found to affect the properties of the polymer. The values of conductivity of the polypyrrole films increased with decreasing electrodeposition temperature and increasing current density. For a 2 cm x 5 cm substrate, the highest conductivity value, 514 S/cm, was obtained with samples prepared at a temperature of -20°C and a current density of 3.0 mA/cm². The ratio of conductivities measured along (aₐlong) and across (aₐcross) the surface of the samples increased with decreasing electrodeposition temperature and current density, but was strongly dependent on the electrode geometry. A conductivity of 996 S/cm and a aₐlong/aₐcross ratio of 3.3 was obtained for a film deposited on a long narrow substrate, compared with a ratio of 1.2 for a square substrate. Films produced in propylene carbonate solvent possessed better properties than when either acetonitrile or another study (18), the maximum conductivity for films produced at room temperature was 279 S/cm, but this rose to 340 S/cm when the deposition temperature was lowered to 0°C.

There has been much interest in the area of conducting polymers over the last decade, and many varieties have been synthesized. Polypyrroles have been widely studied, as they have high conductivity and also good air stability. The properties of conducting polypyrrole films are influenced by a large number of factors. These include the nature and amount of the anion incorporated in the structure (1), deposition potential (2), current density (3), deposition time (4), solvent (5), content of water in the solution (6), and deposition temperature (4, 6, 8-11).

The conductivity of the polymer material is one of the important properties for most electrochemical applications. The conductivity of polypyrrole films has generally been reported to lie within the range of 10-300 S/cm (12-16), although values up to 600 S/cm have also been reported (17).

The effect of deposition temperature for polypyrrole was found to be an important variable in producing conducting films. As has been reported by other workers (4, 6, 9-11) reduction of polymerization temperature substantially improves electrical conductivity. Most previously published results have been obtained at room temperature, although values up to 600 S/cm have also been reported (17).

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