

the increased role of the solvent in the ionization of phenols and benzoic acids causes the ( $\Delta G^\circ/\Delta S^\circ$ ) ratio to approach that of simple electrostatic theory.

A second possible explanation for the deviation of anilinium ions from the predictions of simple electrostatic theory lies in the assumption that nonelectrostatic Gibbs free-energy changes are negligible for symmetrical proton transfer processes. It has been shown in the above discussion that internal enthalpy changes and, hence, internal Gibbs free-energy changes are expected to be larger for anilinium ions than for phenols or benzoic acids. Thus, anilinium ions would be expected to show a greater deviation from simple electrostatic theory than either phenols or benzoic acids.

Recently Taft and coworkers<sup>29</sup> have determined the gas-phase acidities of several 4-substituted pyridinium ions, a system which is expected to be quite similar to anilinium ions. The results of their work clearly show that internal free energy changes are not equal to zero, but rather they are larger than the corresponding free energy changes in aqueous solution. When data are available on gas-phase acidities of anilinium ions, it will be possible more clearly to interpret the results obtained in this study for the ionization of anilinium ions in aqueous solution.

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## Ion Pairing Effects on Electron Transfer Rate Constants by Electron Spin Resonance Fast Exchange Line-Width Studies. Application to Tri-*p*-tolylamine and Phenothiazine Cation System

Soren P. Sorensen<sup>1</sup> and W. H. Bruning\*

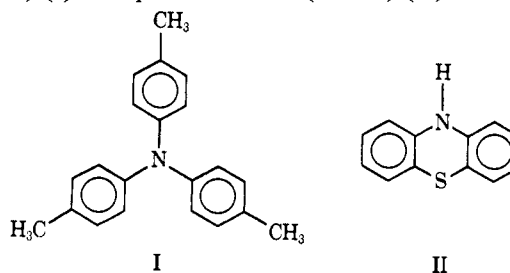
Contribution from the Department of Chemistry, University of Nebraska-Lincoln, Lincoln, Nebraska 68508. Received August 12, 1972

**Abstract:** The rates of electron transfer between radical cations and their parent molecules for tri-*p*-tolylamine and phenothiazine systems have been obtained in various chloroform-acetonitrile mixed solvents in the fast exchange limit, using electrolytic oxidation and chemical oxidation with iodine. The second-order rate constants obtained were solvent dependent, except for the iodine-oxidized tri-*p*-tolylamine systems. The rate constant dependence on the dielectric constant of the solvent was attributed to ion pairing between the organic aromatic cation and the inorganic anion. The solvent independence of the rate constant in the iodine-oxidized tri-*p*-tolylamine systems was attributed to steric factors which prevent various types of ion pair formation. Anomalous activation energies were obtained for systems having extensive ion pairing and were attributed to a shift in equilibria between various types of ion pairs with temperature. The results have obvious significance for reaction mechanism studies in which ion pairs are postulated as intermediates.

Electron spin resonance (esr) provides a convenient method to determine electron transfer rates in organic radical systems. The second-order rate constants for electron transfer in anion and cation exchanging systems have been calculated in the fast exchange region,<sup>2-10</sup> slow exchange region,<sup>10-21</sup> and the inter-

mediate region<sup>8</sup> of exchange. Studies in the fast and slow exchange regions are possible by applying limiting conditions to the full line-shape function for an N site exchanging system.<sup>22</sup> Studies in the intermediate region of exchange are possible by using computer techniques to simulate the esr spectra.<sup>8</sup>

The (esr) hyperfine spectrum of the tri-*p*-tolylamine (TPTA) (I) and phenothiazine (PTAZ) (II) cation sys-



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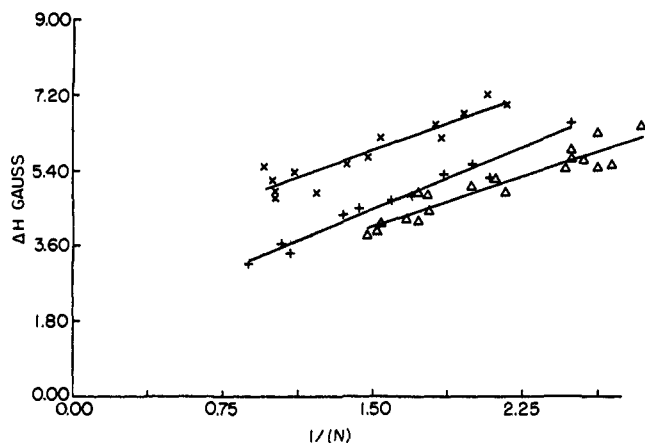


Figure 1. Least-squares plots of line width vs. reciprocal of tri-*p*-tolylamine (TPTA) concentration in moles per liter, electrolytically oxidized: (Δ) 2:1, (+) 3:1, and (×) 5:1  $\text{CHCl}_3\text{-CH}_3\text{CN}$  mixed solvents (0.04 *M* TBAP),  $[\text{TPTA}^+] \leq 10^{-4}$  *M*.

tems are very complex so rate studies are possible only in the region of fast exchange where the spectral hyperfine lines are collapsed into one sharp resonance line. The second-order rate constants were obtained by using the expression<sup>22</sup>

$$k = \frac{2.04 \times 10^7 \nabla}{\Delta H [N]} \quad (1)$$

where  $\nabla$  is the second moment of the unbroadened spectrum in gauss,<sup>2</sup>  $\Delta H$  is the peak-to-peak corrected line width and  $[N]$  is the concentration of neutral diamagnetic material in moles per liter. The rate constants obtained using eq 1 were corrected by the fourth moment correction described by Johnson and Holz.<sup>23</sup> This theoretical correction has been applied to earlier work<sup>9,10</sup> and will not be discussed here.

Second-order rate constants for electron exchange were obtained for (TPTA<sup>+</sup>) and (PTAZ<sup>+</sup>) in various chloroform-acetonitrile solvent mixtures using chemical oxidation by iodine and electrolytic oxidation (0.04 *M* TBAP supporting electrolyte). The methods of oxidation and solvent mixture employed affect the second-order rate constant for electron transfer of some of these systems. Ion pairing models are used to explain these effects. Anomalous apparent activation energies were also obtained for some of these systems and will be discussed.

## Experimental Section

**1. Materials.** Tri-*p*-tolylamine (TPTA) was prepared by the method of Walter.<sup>24</sup> The product obtained from the above method contained oily by-products along with the tertiary amine. This black impurity was removed by several recrystallizations from glacial acetic acid and then vacuum sublimed at its melting point. White crystals with a melting point of 116.5 to 117.5° were obtained and used in the rate studies. Phenothiazine (PTAZ) was commercially obtained and vacuum sublimed. Reagent grade iodine and tetra-*n*-butylammonium perchlorate (TBAP) were used as commercially obtained.

Reagent grade chloroform was purified by removing the ethanol with concentrated  $\text{H}_2\text{SO}_4$  and then washed several times with water. Distillation from  $\text{P}_2\text{O}_5$  keeping the center fraction, followed by storage in a vacuum bottle over Type 4A molecular sieves, completed its purification. Reagent grade acetonitrile was twice dis-

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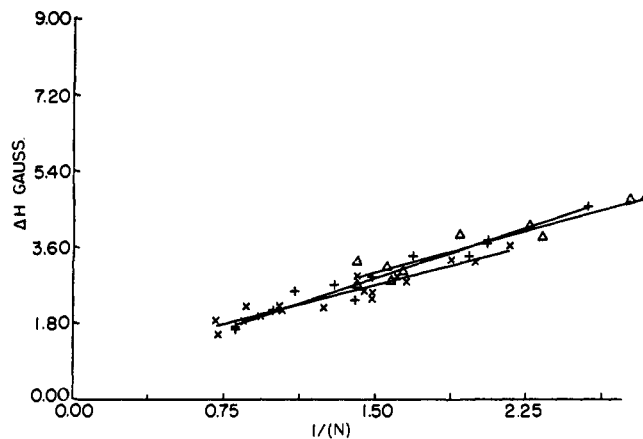


Figure 2. Least-squares plots of line width vs. reciprocal of TPTA concentration in moles per liter, chemically oxidized by iodine: (Δ) 2:1, (+) 3:1, and (×) 5:1  $\text{CHCl}_3\text{-CH}_3\text{CN}$  mixed solvents,  $[\text{TPTA}^+] \leq 10^{-4}$  *M*.

tilled from  $\text{P}_2\text{O}_5$  and a center cut fraction was stored in a vacuum bottle over Type 4A molecular sieves.

**2. Preparation of Cations for Rate Studies.** Each positive ion solution for a rate experiment was prepared in a Pyrex apparatus under reduced pressure. For electrolytic oxidation the appropriate solutions were electrolytically oxidized, with 0.04 *M* TBAP supporting electrolyte, for a time sufficient and with a potential high enough so as to obtain the desired radical concentration (in all cases a current less than 0.5 mA was used). For chemical oxidation, iodine was released into the system in amounts so as to oxidize the desired amount of compound (iodine was the limiting reagent in production of the cation) (see below). In both apparatuses the solution could be directed to an attached probe for experimental measurements. The apparatus used is fully described elsewhere.<sup>25</sup> Visible absorption spectra and esr hyperfine spectra were obtained for the species formed and compared with reported spectra.<sup>26,27</sup> The species generated in each case was thus shown to be the monopositive ion of the appropriate compound ( $\lambda_{\text{max}}$  673 with a shoulder at 580  $\mu\text{m}$  for TPTA<sup>+</sup>;  $\lambda_{\text{max}}$  437 and 512  $\mu\text{m}$  for PTAZ<sup>+</sup>).

**3. ESR Spectrometer.** All esr measurements described were made with a Jeolco-3BSX spectrometer operating near 9.7 kHz, with linear field sweep and 100-kHz field modulation and equipped with a variable temperature cavity. Temperatures were maintained to  $\pm 1^\circ$ . Calibration of the field sweep was achieved by using the 13.07 G esr splitting of peroxyamine disulfonate.

**4. Corrections.** Line shapes of selected spectral lines were examined<sup>28</sup> and found to be very nearly Lorentzian. Spin concentrations of selected samples were examined by comparison with standard 1,1-diphenyl-2-picrylhydrazyl (DPPH) samples in similar solvents and an upper limit of  $10^{-4}$  *M* cation was found in all cases (usually the spin concentration was less), thus suggesting no large corrections were necessary for Heisenberg broadening. If necessary, modulation corrections were made.<sup>29</sup>

## Results

**A. Tri-*p*-tolylamine (TPTA) Systems.** The second-order rate constants for electron exchange in (TPTA) cation systems were obtained using chemical oxidation by iodine and electrolytic oxidation (0.04 *M* TBAP). Because of the relatively low solubility of neutral (TPTA) in acetonitrile, mixed solvents (2:1, 3:1, and 5:1

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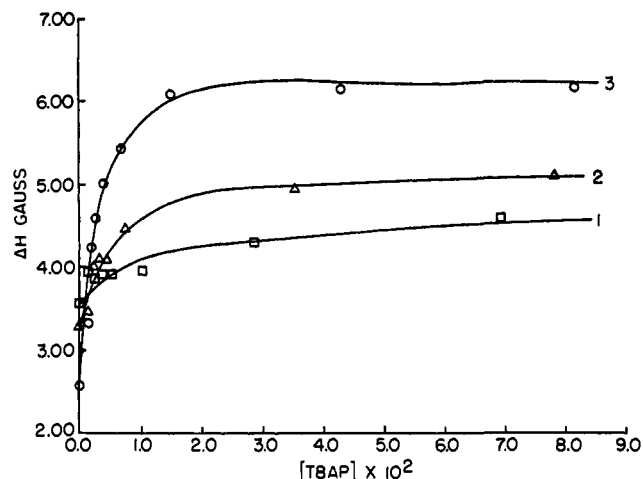


Figure 3. Plots of line width *vs.* tetra-*n*-butylammonium perchlorate concentration in moles per liter: TBAP added to [TPTA]-TPTA<sup>+</sup> iodine-oxidized fast exchange systems with (1) 2:1, (2) 3:1, (3) 5:1 CHCl<sub>3</sub>-CH<sub>3</sub>CN mixed solvent ratios. [TPTA<sup>+</sup>] < 10<sup>-4</sup> M in each case and (1) [TPTA] = 0.54 M, (2) [TPTA] = 0.59 M, (3) [TPTA] = 0.62 M.

CHCl<sub>3</sub>-CH<sub>3</sub>CN) were required in order to attain the concentration needed to completely collapse the spectrum into one sharp spectral line, as is required for fast exchange analysis (eq 1).

In order to use eq 1, the second moment of the uncollapsed hyperfine spectrum must be obtained. The coupling constants for (TPTA<sup>+</sup>) were found to be equal, within experimental error, for the three solvent systems (both iodine oxidized and electrolytically oxidized). Table I gives the coupling constants for the (TPTA)

Table I. Coupling Constants for (TPTA<sup>+</sup>) (gauss)

$A_N = 8.63$	$A_H(\text{ortho}) = 2.10$
$A_H(\text{para}) = 3.93$	$A_H(\text{meta}) = 1.06$

cation systems obtained in this study. The second moment for all the (TPTA<sup>+</sup>) systems using the coupling constants in Table I is 92.68 G.<sup>2</sup>

Figures 1 and 2 show the plot of the peak-to-peak line width *vs.* the reciprocal of the molar concentration of (TPTA). Table II gives the fourth moment corrected second-order rate constants and intercepts obtained from Figures 1 and 2. Although points are plotted for 5:1 CHCl<sub>3</sub>-CH<sub>3</sub>CN electrolytically oxidized solutions in Figure 1, we place minor emphasis on them since these solutions were not significantly concentrated in TPTA to reach the fast exchange region where eq 1 or extensions of this equation were applicable.<sup>23</sup> The points are included to indicate the solvent dependence of this system only.

The increased line widths obtained when (TBAP) is present in (TPTA<sup>+</sup>) systems undergoing electron exchange in the fast exchange region are noted from Figures 1 and 2, and the intercept values given in Table II. This broadening effect was further studied by noting the effect depicted in Figure 3. The three systems, each containing known amounts of neutral amine in 2:1, 3:1, and 5:1 CHCl<sub>3</sub>-CH<sub>3</sub>CN solvent mixtures, were chemically oxidized with iodine (radical concentration was ≤ 10<sup>-4</sup>), and the line widths were obtained as

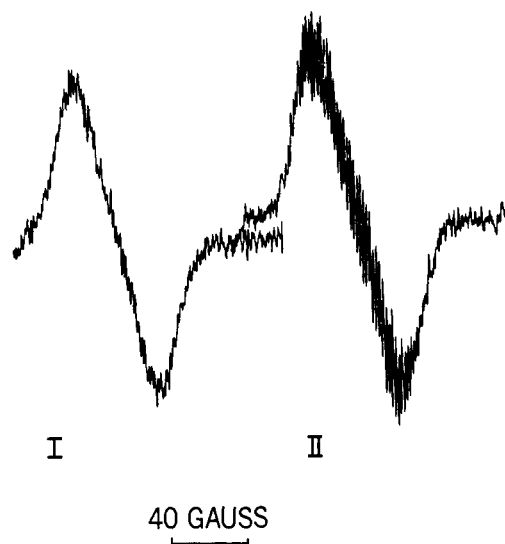


Figure 4. Effect of tetra-*n*-butylammonium perchlorate on Heisenberg spin exchange: (I)  $\sim 3 \times 10^{-3}$  M TPTA<sup>+</sup> ([TPTA] <  $5 \times 10^{-4}$  M), I<sub>2</sub> oxidized in CH<sub>3</sub>CN; (II) same solution, but with [TBAP] = 0.04 M. Note appearance of pronounced hyperfine splittings.

Table II. Rate Constants, Apparent Activation Energies, and Intercepts (TPTA-TPTA<sup>+</sup>)<sup>a,b</sup>

CHCl <sub>3</sub> -CH <sub>3</sub> CN	$k \times 10^{-9}$ , $M^{-1} \text{sec}^{-1}$ <sup>c</sup>	$E_A$ , kcal	$I$ , G
Iodine-Oxidized Systems			
2:1	$0.96 \pm 0.17$	$3.39 \pm 0.68$	$0.98 \pm 0.26$
3:1	$0.94 \pm 0.15$	$3.30 \pm 0.66$	$0.48 \pm 0.20$
5:1	$0.98 \pm 0.18$	$3.99 \pm 0.70$	$0.83 \pm 0.20$
Electrolytically Oxidized Systems			
2:1	$0.66 \pm 0.12$	$0.87 \pm 0.50$	$1.60 \pm 0.28$
3:1	$0.55 \pm 0.11$	$1.89 \pm 0.70$	$1.40 \pm 0.20$
5:1 <sup>d</sup>			

<sup>a</sup> Temperature 18°. <sup>b</sup> Rate constant and activation energy errors are computed estimates; intercept errors are standard deviations from the mean. <sup>c</sup> Fourth moment correction applied. <sup>d</sup> See Results.

successive amounts of (TBAP) were added. Similar line broadening effects were observed if tetra-*n*-butylammonium tetrafluoroborate was used instead of (TBAP); however, (TBAP) was used as the supporting electrolyte in all the systems in this study so it will be the only salt considered.

The effect of (TBAP) on systems undergoing Heisenberg exchange was also studied. To perform this type of experiment, samples of neutral (TPTA) were completely oxidized with excess iodine and then (TBAP) was added (Figure 4).

From the temperature dependence of the second-order rate constants the apparent activation energies of the (TPTA) cation systems were obtained and are given in Table II.

**B. Phenothiazine (PTAZ) Systems.** The second-order rate constants for electron exchange in (PTAZ) cation systems (CH<sub>3</sub>CN and 5:1 CHCl<sub>3</sub>-CH<sub>3</sub>CN solvents) were obtained using chemical oxidation by iodine and electrolytic oxidation (0.04 M TBAP supporting electrolyte). The hyperfine coupling constants for the two solvent systems were used to obtain the second moment of the uncollapsed hyperfine spectrum. We ob-

**Table III.** Rate Constants, Apparent Activation Energies, and Intercepts (PTAZ-PTAZ<sup>+</sup>)<sup>a,b</sup>

Solvent	$k \times 10^{-9}, M^{-1} \text{sec}^{-1}{}^c$	$E_A, \text{kcal}$	$I, \text{G}$
Iodine-Oxidized Systems			
CH <sub>3</sub> CN 5:1 CHCl <sub>3</sub> -CH <sub>3</sub> CN <sup>d</sup>	4.33 ± 0.65	1.45 ± 0.55	0.56 ± 0.29
Electrolytically Oxidized Systems			
CH <sub>3</sub> CN	4.19 ± 0.28	1.67 ± 0.60	0.32 ± 0.24
5:1 CHCl <sub>3</sub> -CH <sub>3</sub> CN	1.80 ± 0.28	1.40 ± 0.55	0.95 ± 0.27

<sup>a</sup> Temperature 18°. <sup>b</sup> Rate constant and activation energy errors are computed estimates; intercept errors are standard deviations from the mean. <sup>c</sup> Fourth moment correction applied. <sup>d</sup> See Results.

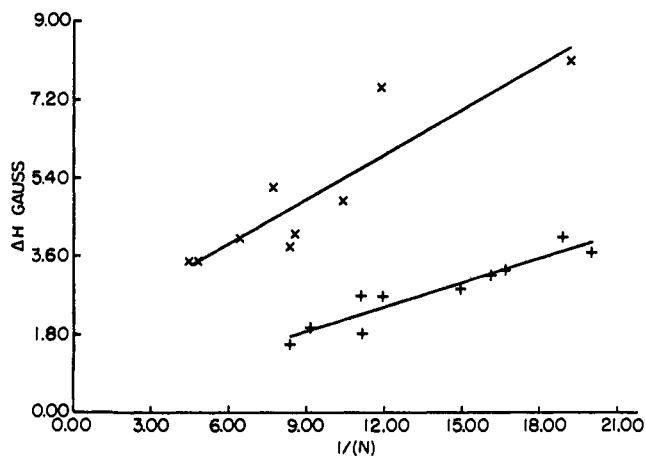


Figure 5. Least-squares plots of line width vs. reciprocal of PTAZ concentration in moles per liter, chemically oxidized by iodine: (+) CH<sub>3</sub>CN, (×) 5:1 CHCl<sub>3</sub>-CH<sub>3</sub>CN solvents, [PTAZ<sup>+</sup>] ≤ 10<sup>-4</sup> M.

tained coupling constants from the CH<sub>3</sub>CN solvent system (both from iodine and electrolytic oxidation) that compared favorably with those reported in the literature.<sup>27b-d</sup> A slight difference was noticed for the coupling constants in the 5:1 CHCl<sub>3</sub>-CH<sub>3</sub>CN mixed solvent systems (performed in this laboratory using both iodine and electrolytic oxidation). The second moments obtained were 46.20 G<sup>2</sup> for the CH<sub>3</sub>CN solvent systems and 45.87 G<sup>2</sup> for the 5:1 CHCl<sub>3</sub>-CH<sub>3</sub>CN solvent systems.

Figures 5 and 6 show the plot of the peak-to-peak line width vs. the reciprocal of the molar concentration of (PTAZ). Table III gives the fourth moment corrected second-order rate constants and intercepts obtained from Figures 5 and 6. The apparent activation energies of the different (PTAZ) cation systems are also given in Table III. Although data are plotted in Figure 5 for 5:1 CHCl<sub>3</sub>-CH<sub>3</sub>CN solutions oxidized by I<sub>2</sub>, eq 1 and its various corrected forms<sup>23</sup> were found inapplicable (see Results, TPTA data). Minor significance should be attached to the curve in Figure 5 except to note its apparent solvent dependency.

## Discussion

**A. Tri-*p*-tolylamine Systems.** An examination of Figures 1 and 2 indicates that the width of the resonance line is dependent on solvent if (TBAP) is present. This is further depicted in Figure 3. This figure shows that as (TBAP) is added to a system undergoing electron exchange between (TPTA) and (TPTA<sup>+</sup>) the single collapsed spectral line broadens to a maximum value, then levels off upon further addition of (TBAP), thus

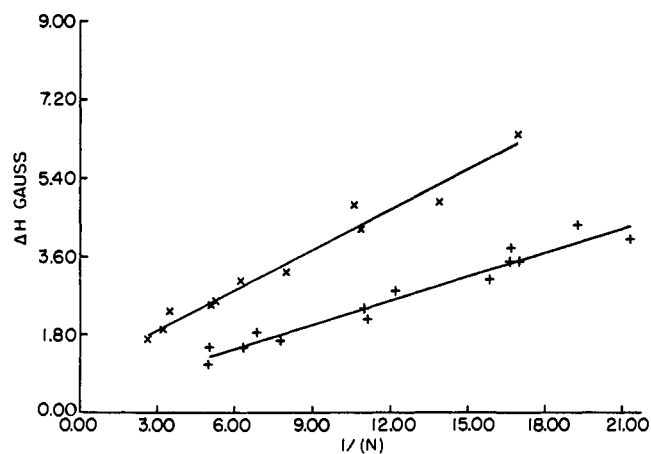


Figure 6. Least-squares plots of line width vs. reciprocal of PTAZ concentration in moles per liter, electrolytically oxidized: (+) CH<sub>3</sub>CN, (×) 5:1 CHCl<sub>3</sub>-CH<sub>3</sub>CN solvents (0.04 M TBAP), [PTAZ<sup>+</sup>] ≤ 10<sup>-4</sup> M.

indicating a direct correlation between the (TBAP) concentration and the resonance line width.

In the region of fast exchange the rate of electron exchange is so rapid that the electron experiences different nuclear spin state environments for only a very short time and an increase in electron exchange rate decreases the line width of the resonance line. Thus in this region, anything that slows the electron exchange process will cause a broadening of the resonance line. An ion pair between (TPTA<sup>+</sup>) and (ClO<sub>4</sub><sup>-</sup>), which could interfere with the formation of the activated complex, could affect the line width in this manner.

Just as electron exchange between the charged species and the neutral precursor will result in uncertainties in the Zeeman levels and thus cause line broadening, collisions between two free radicals in solution leading to an exchange of spins can also result in line broadening. Figure 4 shows the effect of adding (TBAP) to a system undergoing Heisenberg spin exchange.

Since the neutral (TPTA) concentration is very low in this sample (< 5 × 10<sup>-4</sup> M), negligible electron exchange between free radicals and neutral precursor can occur; therefore, the only significant mechanism which can cause line broadening under such dilution is spin exchange as the radicals collide in solution.

In the region of slow exchange the exchanging electrons experience the individual quantum states, but uncertainties result due to the electron exchange so that the individual resonance lines are broadened. The extent of the broadening is dependent on the rate of exchange. Tri-*p*-tolylamine has an extremely complex hyperfine spectrum, and as line broadening begins the spectrum very quickly broadens into very broad

resonance lines (no distinct intermediate region is observed).

Figure 4 shows that as the sample was made 0.04 *M* (TBAP) the amount of hyperfine structure increases, thus indicating that (TBAP) has decreased the rate of spin-spin exchange. An ion pair between (TPTA<sup>+</sup>) and (ClO<sub>4</sub><sup>-</sup>) can again be postulated.

The dielectric constants of the solvents used (CH<sub>3</sub>CN, *D* = 38.0, and CHCl<sub>3</sub>, *D* = 4.8)<sup>30</sup> suggests that the bulk dielectric constants of the CHCl<sub>3</sub>-CH<sub>3</sub>CN solvent mixtures are in the following order: 2:1 > 3:1 > 5:1. Since ion pairing is usually enhanced in lower dielectric constant solvents, one would suspect that an ion pair formed in the lower dielectric constant solvent mixture (5:1) would have a greater influence on the electron transfer process and also on the Heisenberg spin exchange process.

Figure 2 illustrates that the line widths obtained in systems chemically oxidized by iodine are not dependent on solvent. Figure 3 shows that the resonance lines in iodine-oxidized systems are immediately broadened by addition of (TBAP) and are then solvent dependent. Figure 1 also shows the solvent dependence of the line width when TBAP is present. The possibility of ion pairing between (TPTA<sup>+</sup>) and (ClO<sub>4</sub><sup>-</sup>) and also the apparent lack of ion pairing between (TPTA<sup>+</sup>) and the anion formed in iodine-oxidized systems is suggested.

Ion pairing is well known in anion systems and has been the subject of many studies.<sup>2,7,8,15,16</sup> Ahn and Johnson<sup>31</sup> have suggested a type of ion pairing between the *N,N*-dimethylpyrazine cation and the tetrafluoroborate anion to help explain the line shape of the esr spectrum of that cation radical. The association between the tetramethylhydrazine cation and the iodide ion in various solvents has been demonstrated.<sup>21</sup> The affinity of aromatic amine cations and the perchlorate anion has been suggested by reports<sup>24,32-34</sup> of the formation of ammonium perchlorate salts. Thus, some type of association between (TPTA<sup>+</sup>) and (ClO<sub>4</sub><sup>-</sup>) seems highly plausible.

The structure and conformation of (TPTA<sup>+</sup>) and either of the anions noted above (ClO<sub>4</sub><sup>-</sup> or I<sup>-</sup>) are also relevant. From infrared spectral analysis<sup>35</sup> and from electron diffraction measurements<sup>36</sup> it can be inferred that (TPTA<sup>+</sup>) has a planar or almost planar arrangement about the central nitrogen atom corresponding to C-N-C angles close to 120°. The molecular parameters given are:<sup>36</sup> *r*(C-C) = 1.39 ± 0.006 Å, *r*(C-N) = 1.42 ± 0.04 Å, and the out-of-plane twist of the aromatic rings is 47 ± 5°.

The geometry of anions present in our solutions must also be considered. When iodine is used as an oxidizing agent one would assume that it is reduced to I<sup>-</sup> or I<sub>3</sub><sup>-</sup>, if additional iodine is present. The fact

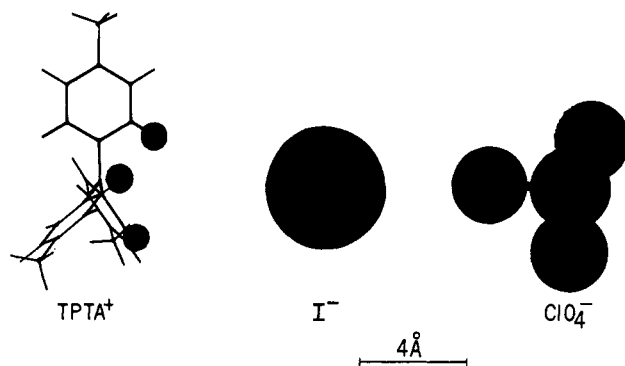


Figure 7. Relative structure of tri-*p*-tolylamine cation and iodide and perchlorate anions.

to be considered in either case is the ionic radius of I<sup>-</sup>, which is 2.20 Å.<sup>30</sup> The perchlorate anion is tetrahedral in solution with oxygen atoms at the corners.<sup>37</sup> The ionic radius of oxygen is 1.42 Å, and the covalent radius would probably be even smaller.

Visualizing the molecular structure of (TPTA<sup>+</sup>), one would assume that the intensity of an ion pairing interaction between it and some anion would depend on the mean distance of closest approach of the anion to the central nitrogen, the center of maximum positive charge density. To approach the central nitrogen the anion would have to pass by the ortho hydrogens on the aromatic rings surrounding the central nitrogen. Figure 7 shows that I<sup>-</sup> or I<sub>3</sub><sup>-</sup> are probably too large to move past the ortho hydrogens in (TPTA<sup>+</sup>) and thus could not approach closely to the central nitrogen, whereas the smaller oxygens at the corners of the tetrahedral (ClO<sub>4</sub><sup>-</sup>) anion are small enough that such obstruction would be less likely.

This could give an indication as to the type of ion pair that could be formed. The ion pair between (TPTA<sup>+</sup>) and the iodide ion could only be very loose, having no, or at the most very slight, solvent dependence in the solvent range in question. The ion pair between (TPTA<sup>+</sup>) and (ClO<sub>4</sub><sup>-</sup>) can be much tighter and a distinct solvent dependence would be expected.

In order for a counterion to affect the rate process, it must somehow participate in the events leading to the formation of the activated complex. In Heisenberg exchange, the gegenion could decrease the number of successful transfer collisions because (1) the complexity of the transition state is exaggerated (possible four particle collision rather than two particle for pairs of the type [ClO<sub>4</sub><sup>-</sup>][TPTA<sup>+</sup>]) or (2) in a tightly paired system, for species with additional bulk due to gegenion-free radical solution sphere interactions, the diffusion-controlled collision rates must be lowered. In each case, however, we are not able to propose an exact mechanism by which the ion pair can affect the formation of the activated complex, but we can only hypothesize that somehow it does. Thus, ion pairing should have the same effect as a decrease in the concentration of spins in a system where Heisenberg spin exchange is occurring or a decrease in the concentration of neutral species in a system where electron exchange is occurring. In the exchange collapsed region, ion pairing has the net effect of driving the system back toward the region

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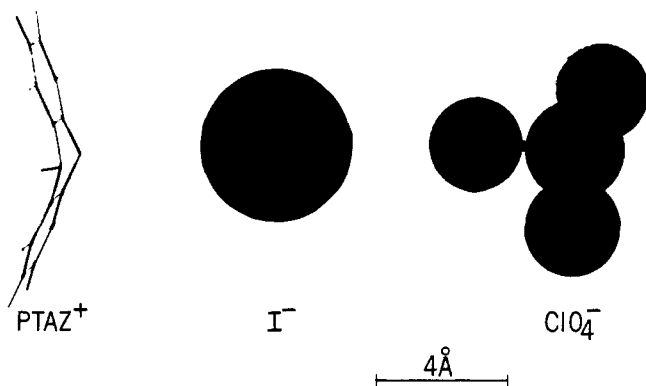


Figure 8. Relative structure of phenothiazine cation and iodide and perchlorate anions.

of slower exchange, so either the line width increases (Figure 3) or hyperfine structure appears (Figure 4).

In the iodine-oxidized systems where the line widths are not solvent dependent, as is shown in Figure 2, one would suspect only very loose ion pairing, and also, because of this the second-order rate constants for each of the solvent mixtures should be the same within experimental error. Table II shows that the corrected second-order rate constants for the iodine-oxidized systems are equal within experimental error.

Hirota, *et al.*,<sup>7</sup> found different types of ion pairs between aromatic anions and alkali metals: loose ion pairs, solvent separated ion pairs, and tight ion pairs. They showed that the second-order rate constant for electron exchange in their systems was smaller for the tighter ion pairs. Since in the region of fast exchange a decrease in the rate of electron exchange results in an increased line width, Figures 1 and 3 would imply that as the dielectric constant of the solvent mixture is decreased, a tighter ion pair between (TPTA<sup>+</sup>) and (ClO<sub>4</sub><sup>-</sup>) and also a slower electron exchange rate would result. Table II shows that the corrected second-order rate constants for the electrolytically oxidized systems follow this trend. The second-order rate constant for the 5:1 CHCl<sub>3</sub>-CH<sub>3</sub>CN solvent system obtained by using eq 1 could not be corrected by fourth moment correction methods as were the 2-1 and 3-1 solvent systems, because the *Z* values for all the data points were beyond the limit which made the fourth moment correction valid.<sup>23</sup> All that can be said about the 5:1 solvent mixture system is that the experimental data points represented experiments too close to the intermediate region of exchange to be used. It should have a second-order rate constant lower than the other electrolytically oxidized systems. Ion pairing in this system was apparently so extensive, due to the low dielectric constant, that the fast exchange region could not be attained.

The second-order rate constants for electron exchange in the electrolytically oxidized systems being less than those for the iodine-oxidized systems, and also the rate constant decrease in going from the electrolytically oxidized system in higher dielectric constant solvent (2:1) to that of lower dielectric constant solvent (3:1), are shown by the corrected second-order rate constants in Table II. This would be expected if ion pairing is a factor.

**B. Phenothiazine Systems.** Table III shows that the corrected second-order rate constants for both the iodine and electrolytically oxidized systems decrease as

the dielectric constant of the solvent is decreased. This would suggest that ion pairing, which is solvent dependent, is occurring in both systems.

The second-order rate constant obtained from the iodine-oxidized 5:1 CHCl<sub>3</sub>-CH<sub>3</sub>CN mixed solvent (PTAZ<sup>+</sup>) system was not used for the same reason that the electrolytically oxidized 5:1 CHCl<sub>3</sub>-CH<sub>3</sub>CN mixed solvent (TPTA<sup>+</sup>) system was not used; *i.e.*, the fast exchange region could not be reached and the proper corrections (Johnson and Holz, ref 23) were invalid. (The data are plotted in Figure 5, but have not been used in the analysis of the effects studied.)

It has been reported that both (PTAZ) and (PTAZ<sup>+</sup>) are folded around the N-S axis.<sup>38</sup> Malrieu, *et al.*,<sup>39</sup> reported that the molecule was folded around the N-S axis by 20 to 40°. Due to the geometry of (PTAZ<sup>+</sup>) (see Figure 8), no structural factor would be present that could prevent the formation of a tight ion pair with the iodide ion as well as the (ClO<sub>4</sub><sup>-</sup>) ion. This could explain the solvent dependence of the second-order rate constant for both the iodine and electrolytically oxidized systems.

Bard, *et al.*,<sup>9</sup> have calculated the second-order rate constant for electron exchange for phenothiazine in acetonitrile using electrolytic oxidation. They reported a fourth moment corrected value of  $6.7 \pm 0.4 \times 10^9$  at 23°. In this laboratory a value of  $4.33 \pm 0.65 \times 10^9$  at 18° was obtained. The temperature at which the data were obtained and the second moments used ( $46.20 \text{ G}^2$  was used in our calculation,  $47.97 \text{ G}^2$  was used for the value reported in ref 9) could explain the discrepancy in the values.

**C. Apparent Activation Energies for (TPTA<sup>+</sup>) and (PTAZ<sup>+</sup>) Systems.** Ion pairing, which is solvent dependent, can have a notable effect on the second-order rate constants in these systems (except the iodine-oxidized (TPTA<sup>+</sup>) systems where steric factors prevent the formation of various types of ion pairs). As the dielectric constant of the solvent is decreased and the expected decrease in the rate constant is observed one would also suspect an accompanying increase in the apparent activation energy. This is not observed. The uncertainties in the low apparent activation energies prevent detailed analysis, but the trend observed, *i.e.*, lower apparent activation energy with lower rate constant, should be noted (see Tables II and III).

Zandstra and Weissman<sup>13</sup> noted that the rate of the electron transfer reaction of sodium naphthalenide-naphthalene in THF increased with a decrease in temperature, thus showing an apparent negative activation energy. Hirota<sup>40</sup> proposed that this peculiarity probably arises from the existence of rapid ion pair equilibria in the system. Hirota, *et al.*,<sup>7</sup> studied several systems and their results were in good agreement with those in ref 13. It was postulated that if the transfer rates for loose ion pairs were much faster than those for tighter ion pairs, and the fraction of loose ion pairs increase rapidly at lower temperatures, the transfer rates may increase at lower temperatures.

The above studies were performed on systems with ion pairing between aromatic organic anions and alkali metal cations. Ion pairing, and thus this type of behavior, should not be ruled out for systems where ion

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pairing occurs between aromatic organic cations and inorganic anions. If the temperature range used to obtain the apparent activation energies in this study was such that, as the temperature is increased, the equilibria between loose and tighter ion pairs is shifted toward an increase in tighter ion pairs, then the line width observed would increase or at least not decrease by the amount expected. The plot of  $\log k$  vs.  $1/T$  would then give a lower slope and thus a lower apparent activation energy. The small temperature range used in this study could prevent the change in sign of  $d \log k/d(1/T)$ , as was observed by the workers in ref 7 and 13, from being detected unambiguously.

Our results would imply that the concentration ratios of different ion pairs do not change rapidly enough with temperature to change the sign of the apparent activation energy, but the anomalous behavior in the  $\log k$  vs.  $1/T$  plot would give low activation energy values.

### Summary and Conclusion

We have determined the second-order rate constants for the (TPTA<sup>+</sup>) and (PTAZ<sup>+</sup>) exchanging cation systems in the region of fast exchange in various solvent mixtures. It was found that the rate constants were solvent dependent (except for iodine oxidized (TPTA<sup>+</sup>) systems). The rate constant dependence on the dielectric constant of the solvent has been attributed to ion pairing between the organic aromatic cation and inorganic anion present. Steric factors which prevent

formation of various types of ion pairs in the (TPTA<sup>+</sup>-I<sup>-</sup>) system have been invoked to rationalize the solvent independence of the rate constants obtained for this system.

The anomalous activation energies obtained for systems having extensive ion pairing have been attributed to a shift in equilibria between various types of ion pairs with temperature.

Organic reactions which proceed *via* an ion-pair intermediate mechanism have been reported.<sup>41</sup> In such reactions attention must be given to the possible types of ion pairs that can result. We have shown in this study that the structure of the species involved in making ion pairs greatly affects the resulting ion pair and in some instances prevents ion pair formation. Structural consideration of the ion pair intermediate should not be overlooked when studying organic reactions which proceed *via* such mechanisms.

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## Electron Spin Resonance of Spin Labels in Organic Inclusion Crystals. Models for Anisotropic Motion in Biological Membranes

G. Bruce Birrell, Shui Pong Van, and O. Hayes Griffith\*

*Contribution from the Institute of Molecular Biology and Department of Chemistry, University of Oregon, Eugene, Oregon 97403. Received September 6, 1972*

**Abstract:** Spin labels have been trapped in organic inclusion crystals in order to examine well-defined examples of anisotropic molecular motion. A single crystal 9.5-GHz esr study of di-*tert*-butyl nitroxide (I) in the thiourea host at room temperature has been performed. The spin Hamiltonian is axially symmetric with principal <sup>14</sup>N coupling constant and *g*-value parameters of  $A_{||} = 6.2 \pm 0.1$  G,  $A_{\perp} = 20.0 \pm 0.1$  G,  $g_{||} = 2.0063 \pm 0.0001$ , and  $g_{\perp} = 2.0059 \pm 0.0001$ . The splitting anisotropy equation derived from the spin Hamiltonian, retaining the pseudo-secular terms, accounts for the angular dependence of the coupling constant within  $\pm 0.1$  G, whereas the first-order treatment accurately predicts the *g*-value anisotropy. By comparing these data with the rigid lattice parameters, it is established that the spin label I is undergoing rapid, large amplitude motion about the molecular *y* axis ( $\tau < 10^{-8}$  sec, where  $\tau$  is the rotational correlation time). A line-shape analysis indicates that molecules of I are remarkably well oriented and the angle of tilt is either zero or very nearly zero. Computer simulations establish the acceptable range of orientation parameters as  $0 \leq \theta_0 \leq 10^\circ$  and  $0 \leq \delta \leq 10^\circ$  where  $\theta_0$  and  $\delta$  are the Gaussian distribution parameter and angle of tilt parameter, respectively. Polycrystalline samples of I in thiourea and 2,2,6,6-tetramethyl-1-oxyl-4-piperidyl dodecanoate (II) in the host  $\beta$ -cyclodextrin are also examined at room temperature and  $-196^\circ$ . The temperature effects are reversible. At room temperature molecules I and II undergo rapid anisotropic motion about the molecular *y* axis and *x* axis, respectively, whereas at  $-196^\circ$  the molecules yield rigid glass esr spectra. The effects of *x*-, *y*-, and *z*-axis anisotropic motion on esr spectra of randomly oriented samples are discussed. ESR line shapes calculated assuming anisotropic motion confirm the predicted and experimental results.

Spin labeling is playing an important role in establishing the fluid nature of membrane model systems and biological membranes.<sup>1</sup> The technique consists of

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