

detailed examination of this question will require data as a function of temperature so that comparisons similar to those made here can be made. Other work involving LFE relationships has been done<sup>22</sup> as a function of

(22) *E.g.*, (a) E. Lieber, C. N. Rao, and T. S. Chao, *J. Amer. Chem. Soc.*, **79**, 5962 (1957); (b) M. E. Langmuir, L. Dodlietti, E. D. Black, and G. Wettermark, *ibid.*, **91**, 2204 (1969).

temperature, but the investigators apparently did not address themselves to this question, nor do their data readily lend themselves to analysis in this manner.

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## Homogeneous Electron-Transfer Reactions of Several Aromatic Anion and Cation Radicals

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**Abstract:** The homogeneous electron-transfer reaction between aromatic molecules and their anion or cation radicals represents one of the simplest possible cases of electron transfer. Although this reaction results in no net chemical change, the rate may be measured by magnetic resonance techniques. This study reports the development of a technique which utilizes *in situ* radical ion generation by electrochemical methods in order to produce radical ion-parent mixtures which may be studied by electron spin resonance techniques in the fast exchange limit. This technique permitted the first large-scale study of the homogeneous exchange rates of radical cations, and reports rate constants for the exchange reactions of phenothiazine, 10-methylphenothiazine, phenoxazine, phenoxathiin, *N,N*-dimethyl-*p*-phenylenediamine, and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine. The effects of substituents upon the exchange rates of several aromatic nitriles were studied; and the effect of solvent variation upon the exchange rate of benzonitrile was determined.

Exchange reactions of all types have long held a fascination for kineticists,<sup>1</sup> and of these electron-exchange reactions have been of especial interest since these processes represent the simplest sort of electron transfer. The publication by Ward and Weissman<sup>2,3</sup> of an electron spin resonance (esr) study of the rate of electron exchange for the naphthalene-sodium naphthalenide system was significant because it presented a measurement technique which did not rely on radioactive tracers and which was applicable to a large number of organic molecules.

The electron-transfer reactions of aromatic anion radicals have been the most extensively studied group since the early work of Ward and Weissman. They have been shown to be influenced by a variety of factors including solvent,<sup>4-6</sup> identity of counterion,<sup>5,6</sup> and the degree of ion pairing between the anion radical and the counterion.<sup>5,6</sup>

Neutral radicals occur far less frequently but rate constants for the electron-transfer reactions of two systems have been obtained. Lown<sup>7a</sup> studied the triphenylmethyl, triphenylmethyl cation electron transfer while Jones and Weissman<sup>7b</sup> examined the effect of counterion and solvent on the reaction of the tris-*p*-

nitrophenylmethyl radical with the tris-*p*-nitrophenyl methide anion.

In spite of the large number of cation radicals that have been observed with esr, it is surprising that so few electron-transfer reactions involving this important class of radicals have been reported. Cross reactions between various aromatic hydrocarbons and their cation radicals have been observed by pulse radiolysis.<sup>8</sup> For the well-known stable cation of tetramethyl-*p*-phenylenediamine (Wurster's Blue cation) three separate investigations<sup>9-11</sup> revealed that the electron transfer occurs primarily between the radical and free amine, even if protonated species are also present. Romans, *et al.*,<sup>12</sup> observed the electron-transfer reaction of the tetramethylhydrazine cation radical complexed with the singly charged anion of molecular iodine with parent tetramethylhydrazine.

The reason for the small number of investigations of cation radicals becomes evident if the requirements for the determination of electron-transfer rate constants using esr are examined. Knowledge of both the parent and radical concentration is a necessity, since the rate constant is determined from the change in line shape of the esr spectrum as the parent-to-radical concentration ratio is varied. The radical concentration must also be kept small enough to prevent spin exchange from becoming an appreciable source of spin

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(6) N. Hirota, R. Carraway, and W. Schook, *ibid.*, **90**, 3611 (1968).

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(9) C. R. Bruce, R. E. Norberg, and S. I. Weissman, *ibid.*, **24**, 473 (1956).

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(12) D. Romans, W. H. Bruning, and C. J. Michejda, *J. Amer. Chem. Soc.*, **91**, 3859 (1969).

relaxation. Success in determining an electron-transfer rate constant thus generally requires both the reproducible preparation of small amounts of radical and the reproducible variation of the parent concentration. While many methods for the chemical preparation of cation radicals are known,<sup>13</sup> the mechanisms are not completely understood and the amount of parent and radical present in a given solution is hard to control. This is the main reason for the small number of investigations of the electron-transfer reactions of cation radicals.

Controlled potential electrolysis, however, can be used for the quantitative preparation of dilute solutions of anion or cation radicals provided that the radical is stable. This has been one of the principal methods used to prepare anion radicals for the investigation of their high-resolution esr spectra.<sup>14,15</sup> Adams and coworkers have used electrochemical generation in their studies of the electron-transfer rates of the anions of several hydrocarbons, nitro compounds, and nitriles<sup>4,16,17</sup> as well as in their work on spin exchange.<sup>18,19</sup>

We have used controlled potential electrolysis in conjunction with the esr fast exchange limit to obtain the electron-transfer rate constants for the cation radicals of the three tricyclic heterocycles phenothiazine, 10-methylphenothiazine, and phenoxazine and the Wurster's Blue cation in acetonitrile. The fast exchange limit was chosen because of the complex high-resolution esr spectra these compounds exhibit.

Using controlled potential electrolysis, samples were prepared by addition of parent to a radical-only solution outside of the esr cavity. This was extremely time consuming and it was obvious that radicals less stable than these cations would be difficult if not impossible to study in this manner.

The search for a technique which would make the study of less long-lived species possible as well as reduce the amount of time needed to study stable radicals revealed that the *in situ* electrolysis<sup>14,20</sup> of concentrated parent solutions was both convenient and accurate. The resulting esr spectra were either in or very near the fast exchange limit and when compared with the results from the controlled potential experiments the agreement was found to be good.

The *in situ* method was successfully employed for studies of the phenoxathiin and dimethyl-*p*-phenylenediamine cation radicals in acetonitrile and the anions of eight substituted benzonitriles, dibenzofuran, dibenzothiophene, and stilbene in dimethylformamide. Additionally the benzonitrile anion was examined in the solvents dimethylformamide, acetonitrile, propylene carbonate, dimethyl sulfoxide, and dioxane.

The series of substituted benzonitriles affords the opportunity to look for a different type of correlation

for electron-transfer rate constants. Rate-constant correlations applied until the present have involved varying some property of the solution such as solvent or counterion.<sup>4-6</sup> For the benzonitriles, however, all experiments were performed using the same solvent and supporting electrolyte so differences in rate constant should be due to the molecular properties of the particular species involved. Similar remarks apply to the four heterocyclic cations.

Accordingly, two types of correlation have been examined. One involves the correlation of rate constant with molecular properties such as oxidation potential, reduction potential, or molecular geometry. The other postulates models in which electron transfer takes place between individual groups of atoms in the radical and parent.

The solvent data are compared with two models for electron transfer. One is the model used in the correlation for the rate constants of the substituted benzonitriles. The other is the well-known theory of Marcus.<sup>21</sup>

## Experimental Section

**Chemicals.** Tetrabutylammonium perchlorate was obtained from Southwestern Analytical Chemicals, dried under vacuum, and stored over calcium chloride. Tetraethylammonium perchlorate was prepared by mixing 500 g of tetraethylammonium bromide in 1500 ml of hot water with 350 g of NaClO<sub>4</sub>·H<sub>2</sub>O in 400 ml of hot water and heated further until the tetraethylammonium perchlorate dissolved. It was recrystallized six times from water and stored over calcium chloride.

Dimethylformamide (Eastman Organic Chemicals) was vacuum distilled from anhydrous copper sulfate at 55°. Acetonitrile (Matheson Coleman and Bell) was stored over calcium hydride for 12 hr and distilled from phosphorus pentoxide at 80° and atmospheric pressure. Acetonitrile was used as a solvent for both anion and cation radicals. All other solvents were used only for anions. Propylene carbonate (Jefferson Chemical Co.) was vacuum distilled at 110°. Dimethyl sulfoxide (Eastman Organic Chemicals) was dried over calcium hydride for 48 hr and vacuum distilled with a nitrogen leak at 68°. Dioxane (J. T. Baker Chemical Co.) was distilled from sodium at 99° and atmospheric pressure.

Phenothiazine, 10-methylphenothiazine, and phenoxathiin (Eastman Organic Chemicals) were chromatographed on an alumina column using benzene and recrystallized from benzene. Phenoxazine was prepared according to Gilman and Moore<sup>22</sup> and twice sublimed *in vacuo*. *N,N,N',N'*-Tetramethyl-*p*-phenylenediamine hydrochloride (Eastman Organic Chemicals) was neutralized with sodium hydroxide, extracted with benzene, chromatographed on an alumina column, and sublimed *in vacuo*. *N,N*-Dimethyl-*p*-phenylenediamine (Eastman Organic Chemicals) was distilled at atmospheric pressure at 259°. The distillate was dark red.

Benzonitrile (Matheson Coleman and Bell) was used as received. Phthalonitrile and terephthalonitrile (Eastman Organic Chemicals) were chromatographed using benzene on an alumina column and recrystallized from benzene.

Pyromellitonitrile was prepared using the method of Lawton and Ritchie.<sup>23</sup> 4-Cyanopyridine (Aldrich Chemical Co.) was chromatographed using benzene and recrystallized from benzene.

*o*-Tolunitrile (Aldrich Chemical Co.) was distilled at atmospheric pressure and 200°. *m*-Tolunitrile (Aldrich Chemical Co.) was distilled at atmospheric pressure and 210°. *p*-Tolunitrile was distilled at atmospheric pressure and 210°.

Dibenzothiophene and dibenzofuran (Eastman Organic Chemicals) were chromatographed on alumina using benzene and recrystallized from benzene.

## Radical Ion Generation

The cation radicals of phenothiazine, 10-methylphenothiazine, phenoxazine, and *N,N,N',N'*-tetramethyl-*p*-

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(15) R. N. Adams, *J. Electroanal. Chem.*, **8**, 151 (1964).

(16) P. Ludwig and R. N. Adams, *J. Chem. Phys.*, **37**, 828 (1962).

(17) T. Layloff, T. A. Miller, R. N. Adams, H. Fah, A. Horsfield, and W. Proctor, *Nature (London)*, **205**, 382 (1965).

(18) T. A. Miller, R. N. Adams, and P. N. Richards, *J. Chem. Phys.*, **44**, 4022 (1966).

(19) T. A. Miller and R. N. Adams, *J. Amer. Chem. Soc.*, **88**, 5713 (1966).

(20) L. H. Piette, P. Ludwig, and R. N. Adams, *Anal. Chem.*, **34**, 916 (1962).

phenylenediamine (Wurster's Blue) were studied by external generation. They were chosen because previous esr and electrochemical studies indicated suitable stability.<sup>24</sup> Acetonitrile was employed as the solvent. The supporting electrolyte was tetraethylammonium perchlorate (TEAP), used at a concentration of 0.1 *M* for all samples.

The cell used most often was similar to one originally designed by Sadler.<sup>25</sup> Another cell with only one sidearm was also used. The solvent and supporting electrolyte were degassed at least once before a helium atmosphere was introduced in the cell. This atmosphere was maintained for the duration of the period in which samples were taken.

The sample was introduced and the controlled potential electrolysis was performed using a potentiostat designed by Bard.<sup>26</sup> The concentration of the electroactive species ranged from  $5 \times 10^{-4}$  to  $10^{-3}$  *M*. The potentials vs. the saturated calomel electrode (sce) were 0.80 V for phenothiazine and 10-methylphenothiazine, 0.65 V for phenoxazine, and 0.40 V for Wurster's Blue. The total number of coulombs passed was measured using a voltage-to-frequency converter-digital counter described by Bard and Solon.<sup>27</sup> An sce was used as the standard electrode while the working electrode was a platinum gauze with a platinum wire as the auxiliary electrode.

For each system at least one radical-only sample was taken after the conclusion of electrolysis and its spectrum was compared with those in the literature. The radical-parent solutions were prepared using a mixing chamber which was evacuated for approximately 15–30 min after introduction of a known amount of the solid parent. An aliquot of the radical solution was drawn into the calibrated barrel. After complete dissolution the solution was admitted to the sample tube, which had also been previously evacuated. The sample tube was then immersed in liquid nitrogen and removed with a torch.

The external method provided a reliable means of measuring electron-transfer rates but suffered from several disadvantages. The process was somewhat unwieldy and time consuming. An average of 1 hr was necessary to obtain a sample, with at least half of this time required to dissolve the solid parent due to the high concentrations involved. The number of operations increased the probability of admission of oxygen to the sample, leading to line broadening. Destruction of the radical was also possible.

Additionally, if the lifetime was short the number of samples obtainable from a given electrolysis decreased, necessitating the repetition of the lengthy preelectrolysis and electrolysis procedures in order to secure a sufficient amount of data.

The *in situ* electrolysis of organic molecules has been utilized extensively in studying the high-resolution esr spectra of the resulting radical ions.<sup>14,20</sup> Ludwig and Adams also used it to study the electron-transfer reaction of the benzonitrile anion radical in the slow

exchange limit.<sup>16</sup> They observed but did not analyze singlets for two samples of fairly high benzonitrile concentration. This indicated the possibility of using *in situ* electrolysis with the fast exchange method. This approach was used for the entire group of anions and the phenoxathiin and *N,N*-dimethyl-*p*-phenylenediamine cations as well as a few preliminary experiments on the phenoxazine cation radical.

The electrolysis cell was the Varian flat cell Model 4556. A Heathkit voltage regulated power supply was used with a platinum gauze anode and a platinum wire cathode for oxidations while a mercury pool cathode and a silver wire anode were used for reductions. Current was monitored using a Simpson Model 260 VOM. Solutions were prepared in 5-ml volumetric flasks and were gently stirred with solvent-saturated nitrogen during dissolution of the parent and supporting electrolyte. The supporting electrolyte was tetrabutylammonium perchlorate and its concentration was 0.1 *M* for all samples.

The current level in all experiments was held between 200 and 400  $\mu$ A. At this level a 30-min electrolysis consumed approximately  $3 \times 10^{-6}$  mol of parent. Since 5 ml of about 1 *M* solution was normally used, depletion due to electrolysis was less than 1%.

Stirring with nitrogen was used in the electrolysis cell to avoid high localized concentrations of radical. The nitrogen was passed over hot copper filings and bubbled through a reservoir of solvent before entering the cell through a capillary placed at the top of the flat portion. At the conclusion of electrolysis, if stable enough, the radical's color would be uniformly distributed throughout the cell, showing the effectiveness of the stirring.

This arrangement did not allow the monitoring of the cell potential. To be sure the desired radical was indeed being formed, dilute solutions of the parent compound were electrolyzed under the same conditions used for the electron-transfer experiments. The resulting highly resolved esr spectra were found to agree with those in the literature. Additionally, the current for these generations was intentionally kept low (200–400  $\mu$ A) to avoid excessively negative potentials. The reduction potentials for the parent compounds used were all between  $-1$  and  $-3$  V. The high concentrations of electroactive species provided an effective buffer for potential so excessively positive or negative potentials and their concomitant complications were avoided.

As further proof that the desired radical and not some other species was being generated, it should be noted that with the parent concentration as the only variable, the esr line width systematically narrowed. A final check of the validity of the method was provided by examining several phenoxazine samples using the *in situ* technique. Their line widths were consistent with those obtained by external generation.

Radical concentrations in the flat portion of the cell were shown to be insufficient for spin exchange. Electrolysis was terminated for particularly intense singlets and the line width was observed while the signal amplitude dropped. The data given in Table I for samples of the phenoxazine cation and the stilbene anion show no change within experimental error after stopping electrolysis. The stilbene sample shows less than 1% change in line width for a tenfold increase in gain and a

(24) (a) J.-P. Billon, *Ann. Chim. (Paris)*, **7**, 183 (1962); (b) J.-P. Billon, G. Cauquis, and J. Combrisson, *J. Chim. Phys.*, **374** (1964); (c) S. Odier and F. Tonnard, *ibid.*, **382** (1964); (d) J.-M. Lhoste and F. Tonnard, *ibid.*, **678** (1966); (e) B. M. Latta and R. W. Taft, *J. Amer. Chem. Soc.*, **89**, 5172 (1967).

(25) J. L. Sadler, Ph.D. Dissertation, University of Texas, 1967.

(26) A. J. Bard, *Anal. Chem.*, **35**, 1125 (1963).

(27) A. J. Bard and E. Solon, *ibid.*, **34**, 1181 (1962).

**Table I.** Line Width as a Function of Time for the Stilbene Anion and Phenoxazine Cation

$\Delta H$	Time (min) from first measurement	Signal level	Modulation amplitude
Stilbene Anion Radical, $C^{-1} = 1.48$			
1.08	0	100	1.6
1.05	4	100	1.6
1.08	6.5	100	1.6
1.08 <sup>a</sup>	9	100	1.6
1.08	35	1000	10
1.10	36	1000	10
1.05	38	1000	10
1.08	41	1000	10
Phenoxazine Cation Radical, $C^{-1} = 3.88$			
1.75	0	630	4
1.77 <sup>a</sup>	5	630	4
1.75	19.5	400	3.2
1.70	22.5	400	3.2
1.65	26	400	3.2
1.72	31	400	3.2
1.70	35.5	800	4
1.70	39	800	4
1.72	42	800	4
1.68	45	800	4
1.68	48.5	800	4

<sup>a</sup> Electrolysis stopped after this measurement.

sixfold increase in modulation amplitude over a period of about 40 min. The increase in modulation amplitude easily accounts for the slight broadening observed.

**Esr Measurements.** All esr measurements were made at  $23 \pm 2^\circ$  using a Varian Associates V-4502 spectrometer employing 100-Kc modulation.

Line widths were measured between points of extreme slope in a first derivative presentation. A minimum of four spectra was averaged for each sample. The standard deviation in line width for a given sample was usually about 2-3% with only a few as large as 5%. The field scan rate ranged between 2.5 G/min and 0.5 G/min with the majority of runs (about 80%) being made at 1 G/min. A change in scan rate did not produce appreciable differences in line width.

Where necessary, corrections were made for the contribution of the modulation amplitude to the experimental line width. The effect of modulation amplitude on line width and intensity has been discussed by several authors.<sup>28,29</sup> The true line width is related to the experimentally observed line width for the spectrometer used in these studies by

$$\Delta H = \Delta H_{\text{exp}} - 0.002(\text{MS})$$

where MS is the modulation amplitude machine setting. This relation was obtained from a calibration made employing the perylene anion radical.<sup>30</sup> For most experiments the correction was 0.02 G or less.

For samples in the fast exchange limit the lines were Lorentzian in shape within experimental error using the derivative curve-slope method and the normalized plot method.<sup>31</sup>

(28) G. K. Fraenkel in "Physical Methods of Organic Chemistry," Vol. 1, Part IV, 3rd ed, A. Weissberger, Ed., Interscience, New York, N. Y., 1960, Chapter XLII.

(29) J. E. Wertz and J. R. Bolton, "Electron Spin Resonance," American Chemical Society Short Course 107, Appendix 6.

(30) I. B. Goldberg, private communication.

(31) R. S. Alger, "Electron Paramagnetic Resonance: Techniques and Applications," Interscience, New York, N. Y., 1968, pp 42-44.

The theoretical basis for the determination of exchange rates from line widths has been discussed in the past;<sup>32</sup> however, certain comments pertinent to this type of measurement should be made at this time. The original measurements of Ward and Weissman<sup>2,3</sup> were made at the slow exchange limit where one measures the broadening of an individual hyperfine line. This is severely complicated by overlap in the case of complex spectra. This problem has been treated<sup>33</sup> and rate constants have been determined utilizing computer simulation.<sup>12</sup> Chang and Johnson,<sup>34</sup> however, have shown that measurement in the fast exchange limit is a less complicated approach for these molecules since the spectrum has narrowed to a singlet. In this limit the probability of electron transfer per unit time is much greater than the frequency separation of the resonance lines, *i.e.*

$$\omega_i - \omega_j \ll 1/T_{2i} + 1/\tau \quad (1)$$

where  $\tau$  is the mean radical lifetime between electron transfers,  $1/T_{2i}$  is the line width of the *i*th resonance in the absence of electron transfer, and  $\omega_j$  is the resonance frequency of the *j*th line. The general equation for electron exchange may then be expressed as

$$I(\omega) = \text{Re} \left[ \frac{\gamma H_1 M_0 T_2(\text{eff})}{1 + i(\langle \omega \rangle - \omega) T_2(\text{eff})} \right] \quad (2)$$

where

$$\frac{1}{T_2(\text{eff})} = \frac{1}{T_2^0} + (\langle \omega^2 \rangle - \langle \omega \rangle^2) \left[ \frac{\tau T_2^0}{T_2^0 + \tau} \right] \quad (3)$$

$$\langle \omega \rangle = \sum_i p_i \omega_i \quad (4)$$

and

$$\langle \omega^2 \rangle = \sum_i p_i \omega_i^2 \quad (5)$$

and where  $\gamma$  is the electronic gyromagnetic ratio,  $H_1$  is the magnitude of the oscillating microwave field,  $M_0$  is the equilibrium magnetic moment,  $p_i$  is the fractional population of the *i*th state, and  $\omega$  is the frequency of  $H_1$ .

The quantities  $\langle \omega \rangle$  and  $\langle \omega^2 \rangle$  are obtained from the spectrum in the absence of electron transfer. Since first-order spectra are symmetrical,  $\langle \omega \rangle$  measured in gauss is simply the value of the magnetic field at the spectrum's center and is independent of the hyperfine coupling constants. The quantity  $\nabla = \langle \omega^2 \rangle - \langle \omega \rangle^2$  is the second moment of the spectrum and depends only on the hyperfine coupling constants. Expressed in (gauss)<sup>2</sup> the second moment is

$$\nabla = \sum_i p_i H_i^2 \quad (6)$$

where  $H_i$  is the magnetic field at which the *i*th resonance takes place.

Using the valid approximation  $T_2^0 \gg \tau$ , the line width in gauss of the Lorentzian singlet is

$$\Delta H = \Delta H_0 + 2.05 \times 10^7 \nabla / k[R] \quad (7)$$

where  $\Delta H_0$  is the common line width assumed for all lines in the absence of electron transfer. As before,

(32) C. S. Johnson, Jr., *Advan. Magn. Resonance*, 1, 33 (1965).

(33) J. R. Norris, Jr., *Chem. Phys. Lett.*, 1, 333 (1967).

(34) R. Chang and C. S. Johnson, Jr., *J. Amer. Chem. Soc.*, 88, 2338 (1966).

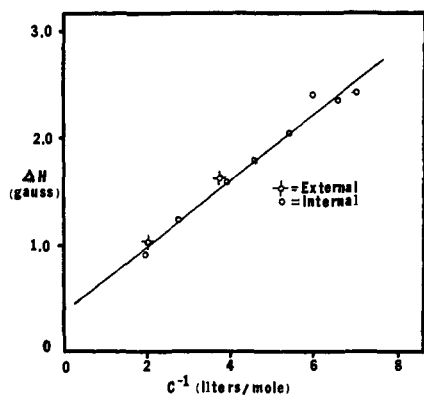


Figure 1. Line widths for external and internal generation of phenoxazine cation.

line width is measured between points of extreme slope in a first derivative presentation.

A few additional comments on the second moment are in order. The quantity  $\nabla$  which arises when the general expression is expanded in the fast exchange limit is the stick spectrum approximation to the true second moment. Chang and Johnson<sup>35</sup> suggested that the second moment could be obtained by overmodulating an uncollapsed spectrum. They measured such a quantity for the stilbene anion radical and obtained good agreement with the stick spectrum result. This would be the true second moment since it takes the finite width of the individual lines into account.

The line shape usually assumed for organic radicals in solution is the Lorentzian line shape.<sup>36</sup> This presents an interesting complication, since the second moment of a Lorentzian line is infinite and any spectrum composed of Lorentzian lines would have an infinite second moment. The precise confirmation of a given line shape becomes difficult after one goes a few line widths into the wings<sup>37</sup> and if one assumes the line shape follows Lorentzian behavior when it can be measured and is zero elsewhere, a finite second moment can be calculated for the "truncated" Lorentzian lines.<sup>38</sup> The results of the calculations indicate that the difference between the stick spectrum second moment and the second moment for Lorentzian lines truncated five line widths from the center is small. This means the experimental determination of a second moment is probably possible but extreme care must be taken.

The appearance of a singlet does not guarantee that the fast exchange limit has been achieved, a situation which may often occur due to the limited solubility of some organic compounds. Johnson and Holz<sup>39</sup> have studied the limits for which eq 7 is applicable and have added a correction that allows rates to be determined outside of the rigorous fast exchange limit. The corrected equation is

$$\Delta H_{\text{ex}} = \frac{2.05 \times 10^7 \nabla}{k[R]} \left[ 1 + \frac{3.16 \times 10^{14} \nabla X}{k^2 [R]^2} \right] \quad (8)$$

(35) R. Chang and C. S. Johnson, *J. Chem. Phys.*, **46**, 2314 (1967).

(36) A. Hudson and G. R. Luckhurst, *Chem. Rev.*, **69**, 191 (1969).

(37) J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, **41**, 949 (1964).

(38) C. P. Poole, Jr., "Electron Spin Resonance," Interscience, New York, N. Y., 1967, pp 807-811.

(39) C. S. Johnson, Jr., and J. B. Holz, *J. Chem. Phys.*, **50**, 4420 (1969).

where

$$X = 2 - \Phi/\nabla \quad (9)$$

The quantity  $\Phi$  is the fourth moment of the esr spectrum in (gauss)<sup>4</sup> and is

$$\Phi = \sum_i p_i H_i^4 \quad (10)$$

The parameter that determines whether a series of measurements is within the fast exchange limit is

$$Z = \left( \frac{3}{4\nabla} \right)^{1/2} \Delta H_{\text{ex}} \quad (11)$$

If  $Z \leq 0.2$ , the fast exchange equation can be used with a maximum error of 5%, while if  $Z \leq 0.4$ , the same maximum occurs if the corrected equation is employed. The largest tolerable line width for either approximation is easily calculated once the second moment is known.

A small value of  $X$  will cause the extended equation's correction to be small, allowing the fast exchange formula to be used for  $Z$  as large as 0.3 or 0.4 with no large introduction of error.

The following procedure was used to obtain a rate constant from a series of line width measurements. Assuming  $Z = 0.2$ , the maximum value of  $\Delta H_{\text{ex}}$  for the fast exchange limit was calculated using eq 11. If a reasonable number of line widths were equal to or smaller than this value, a least-squares analysis was performed to determine a slope and intercept. If line width is plotted *vs.* inverse parent concentration, the rate constant can then be determined using eq 7 in the form

$$k = 2.05 \times 10^7 \nabla / \text{slope} \quad (12)$$

Standard deviations for rate constants were calculated by subtracting the intercept from each line width and calculating the rate constant for each point using eq 7 directly.

If a large percentage of the line widths were larger than the maximum fast exchange line width, the extended equation was used. Even though the fast exchange limit was not being obeyed, the slope of a least-squares analysis yielded an initial estimate of the rate constant. If  $X < 1$ , this would be too high while if  $X > 1$ , it would be too low. The final value was obtained by comparison of experimental line width *vs.* inverse concentration curves with those calculated for different values of the rate constant. No standard deviations were calculated for these systems but they are assumed to be no greater than those in the fast exchange limit. Additionally, a linear correlation coefficient has been calculated for systems in the fast exchange limit.

## Results

Plots of experimental data are given in Figures 1 and 2. Figure 1 shows the data for the phenoxazine system which is representative of those for which it is possible to use the fast exchange equation without correction. In this case  $Z$  was no larger than 0.21 for any line. Figure 2 shows the data for the benzonitrile system in dimethylformamide. The factor  $X$  is small ( $-0.09$ ) for this anion. This causes the correction to the fast exchange expression to be only 1% for  $Z = 0.32$ , corresponding to the lowest parent concentration

**Table II.** Rate Constants, Second Moments, and Correlation Coefficients for Cations

Molecule	Solvent	Supporting electrolyte	Second <sup>a</sup> moment	Ref	Correlation coefficient	$k^b$
Phenothiazine	ACN <sup>c</sup>	TEAP <sup>d</sup>	47.97	40	0.99	$6.7 \pm 0.4 \times 10^9$
10-Methylphenothiazine	ACN	TEAP	75.16	24c		$2.2 \pm 0.3 \times 10^9$
Phenoxazine	ACN	TEAP	67.80	24d	0.99	$4.5 \pm 0.3 \times 10^9$
		TBAP <sup>e</sup>				
Phenoxathiin	ACN	TBAP	2.97	41	0.99	$3.6 \pm 0.2 \times 10^8$
<i>N,N,N',N'</i> -Tetramethyl- <i>p</i> -phenylenediamine	ACN	TBAP	206.12	24e		$1.0 \pm 0.2 \times 10^9$
<i>N,N</i> -Dimethyl- <i>p</i> -phenylenediamine	ACN	TEAP	161.60	24e		$7.5 \pm 0.8 \times 10^8$

<sup>a</sup> The second moment's units are (gauss)<sup>2</sup>. <sup>b</sup> The rate constant's units are liter/(mole second). <sup>c</sup> Acetonitrile. <sup>d</sup> Tetraethylammonium perchlorate. <sup>e</sup> Tetrabutylammonium perchlorate.

**Table III.** Rate Constants, Second Moments, and Correlation Coefficients for Anions

Molecule	Solvent	Supporting electrolyte	Second <sup>a</sup> moment	Ref	Correlation coefficient	$k^b$
Benzonitrile	DMF <sup>c</sup>	TBAP <sup>f</sup>	27.43	42	0.99	$5.6 \pm 0.3 \times 10^8$
Benzonitrile	ACN <sup>d</sup>	TBAP	27.43	42	0.92	$6.6 \pm 0.6 \times 10^8$
Benzonitrile	DMSO <sup>e</sup>	TBAP	27.43	42	0.98	$3.9 \pm 0.4 \times 10^8$
Benzonitrile	Propylene carbonate	TBAP	27.43	42	0.99	$2.6 \pm 0.2 \times 10^8$
Benzonitrile	Dioxane	TBAP	27.43	42	0.92	$1.7 \pm 0.3 \times 10^8$
Phthalonitrile	DMF	TBAP	12.70	42	0.98	$1.2 \pm 0.1 \times 10^9$
Terephthalonitrile	DMF	TBAP	6.90	42	0.99	$1.4 \pm 0.04 \times 10^9$
Pyromellitonitrile	DMF	TBAP	4.14	42	0.96	$9.1 \pm 1.0 \times 10^8$
4-Cyanopyridine	DMF	TBAP	29.46	42	0.95	$6.8 \pm 0.6 \times 10^8$
<i>p</i> -Tolunitrile	DMF	TBAP	75.20	42	0.99	$7.8 \pm 0.5 \times 10^8$
<i>m</i> -Tolunitrile	DMF	TBAP	25.64	43	0.99	$5.6 \pm 0.6 \times 10^8$
<i>o</i> -Tolunitrile	DMF	TBAP	34.71	43	0.99	$8.6 \pm 1.0 \times 10^8$
Dibenzothiophene	DMF	TBAP	24.78	44	0.94	$1.2 \pm 0.1 \times 10^9$
Dibenzofuran	DMF	TBAP	26.12	44	0.98	$1.6 \pm 0.2 \times 10^9$
<i>trans</i> -Stilbene	DMF	TBAP	23.70	45		$1.0 \pm 0.1 \times 10^9$

<sup>a</sup> The second moment's units are (gauss)<sup>2</sup>. <sup>b</sup> The rate constant's units are liters/(mole second). <sup>c</sup> Dimethylformamide. <sup>d</sup> Acetonitrile. <sup>e</sup> Dimethyl sulfoxide. <sup>f</sup> Tetrabutylammonium perchlorate.

used. Johnson and Holz<sup>39</sup> found that the true line width was approximated within 1% by the fast exchange expression for the radicals with  $X \sim 0$  up to  $Z = 0.30$ , showing that the correction to the fast exchange expression is indeed valid for larger  $Z$  values when  $X$  is small and that no additional corrections need be introduced. The same second moment was used when analyzing the data in other solvents. This was done since there was essentially no difference between the high resolution spectra obtained in dimethylformamide and dioxane.

Table II summarizes the data for the cation radicals studied and Table III presents the anion radical data. Those systems for which no correlation coefficient is shown were treated by the extended equation. The reference column gives the source of the hyperfine splitting constants used to calculate various moments.<sup>40-45</sup>

Exchange rates determined in identical solvents have previously been reported for two of these molecules, stilbene and *N,N,N',N'*-tetramethyl-*p*-phenylenedi-

(40) Interpretation of high-resolution spectrum obtained during course of this work. Results differed slightly from other workers, *i.e.*, ref 24c,d, 41.

(41) P. D. Sullivan, *J. Amer. Chem. Soc.*, **90**, 3618 (1968).

(42) P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *ibid.*, **85**, 683 (1963).

(43) A. Lomax, private communication.

(44) R. Gerdil and E. A. C. Lucken, *J. Amer. Chem. Soc.*, **87**, 213 (1965).

(45) A. E. J. Forno, M. E. Peover, and R. Wilson, *Trans. Faraday Soc.*, **66**, 1322 (1970).

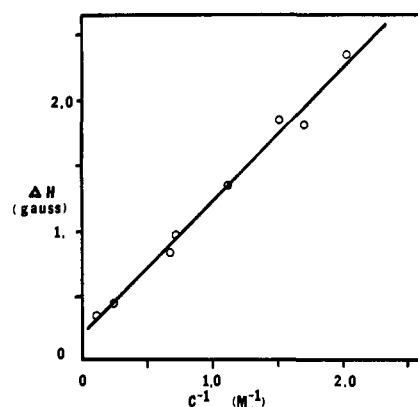


Figure 2. Fast exchange plot for benzonitrile anion.

amine, and those results should be compared. Correct analysis of the stilbene data definitely required the extended equation, changing the rate constant from  $1.3 \times 10^9$  for the fast exchange approximation to  $1.0 \times 10^9$  for the extended equation, the difference being larger than the experimental error. This value is in good agreement with the value of  $1.04 \times 10^9$  obtained by Peover, *et al.*,<sup>45</sup> using the fast exchange limit in the same solvent at the same concentration of supporting electrolyte. The only minor difference was their use of tetrabutylammonium iodide. This result, in fact, verifies their rate constant which was obtained using a straight line drawn through two points, only one of

which was rigorously in the fast exchange limit. They also reported a slow exchange rate constant of  $1.02 \times 10^9$ .

The Wurster's Blue cation also required use of the extended equation, giving a rate constant of  $(1.0 \pm 0.2) \times 10^9$ . This differs by more than experimental error from the value  $(2.0 \pm 1.0) \times 10^8$  determined by Johnson<sup>10</sup> using nuclear magnetic resonance. However, he notes that the error in his calculations is large because Wurster's Blue is a fairly poor example to use for the approximations he employed to obtain his rate constant from experimental data.

## Discussion

**Correlation of Rate and Structure.** One of the main objectives of this research was to study systematically a group of related compounds under similar conditions and interpret the change in electron-transfer rate constant from molecule to molecule in terms of the electronic structure of the species involved. Two groups of compounds have been examined that provide sufficient data for interpretation and speculation.

The first group contains the cation radicals of phenothiazine, 10-methylphenothiazine, phenoxazine, and phenoxathin. The second, larger group comprises the anions of benzonitrile, phthalonitrile, terephthalonitrile, pyromellitonitrile, 4-cyanopyridine, *o*-tolunitrile, *m*-tolunitrile, and *p*-tolunitrile. The anions of dibenzofuran and dibenzothiophene have also been studied and where possible will be compared with the nitrile anions.

Other workers have correlated electron-transfer rate constants with some property of the solvent. Adams and coworkers<sup>4</sup> studied the nitrobenzene anion in the mixed solvent DMF-H<sub>2</sub>O, as well as a series of substituted nitrobenzenes in dry DMF. The general trend observed was that as the nitrogen coupling constant decreased, the electron-transfer rate constant increased. They tentatively suggested "that the more highly localized the unpaired electron perhaps the less effective are collisions in terms of orbital overlap leading to electron transfer."<sup>4</sup> Hirota, Carraway, and Schook<sup>6</sup> studied the electron- and atom-transfer reactions of the naphthalene anion radical prepared by reduction with a variety of alkali metals in ethereal solvents. They showed that the rate constants for both the tight and loose ion pairs increase with increasing temperature but when rapid interconversion between the two takes place, the apparent rate constant may increase with decreasing temperature.

While Hirota's studies<sup>6</sup> coupled with the earlier work of Zandstra and Weissman<sup>5</sup> and Ward and Weissman<sup>3</sup> have shown ion pairing to have marked effects on electron-transfer rate constants, it will not be invoked here to explain differences in rate between the related compounds in the two groups. This is because our measurements for the two groups of compounds, including the solvent studies for benzonitrile with the exception of dioxane, have been made in solvents of high dielectric constant with the same concentration of tetraalkylammonium perchlorates. Conflicting reports<sup>46,47</sup> exist concerning the existence of a tetraalkylammonium ion effect upon hyperfine coupling con-

stants. However, it is clear that this effect is not conventional ion pairing.<sup>47</sup> The butyl derivative was used for all anion radicals while the ethyl derivative was used for all cations except Wurster's Blue. For the phenoxazine cation radical both were used, with the *esr* line widths being mutually consistent.

In the following discussion two general types of correlation will be used. One deals with a property of an entire molecule such as electrochemical reduction potential or the energy of a particular molecular orbital while the other is concerned with the role of specific atoms or groups of atoms within the radical.

The electron involved in the electron-transfer reactions of the anion radicals considered here resides in the lowest lying antibonding orbital while that for the cations is in the highest occupied bonding orbital. The ability of a neutral parent to accept an electron should be a measure of the rate constant for the anion radicals while the ease by which an electron can be removed from a neutral parent should be indicative of the relative electron-transfer rates for cation radicals.

This immediately suggests several quantities which can be measured or calculated which can be correlated with the electron-transfer rate constants. The ability of a molecule to accept an electron is related to its electron affinity which in simple molecular orbital theories is set equal to the negative energy of the lowest lying unoccupied orbital of the parent molecule. Since the same theory predicts a correlation between half-wave potentials for electrochemical reduction and the energy of the pertinent molecular orbital,<sup>48</sup> the rate constant for anion radicals should be correlated with this energy as well as the half-wave potential. Similar arguments should apply to cation systems and oxidation potentials.<sup>48</sup>

The phenothiazine and related cations will be considered first. Table IV gives the HMO energy of the

Table IV. Correlations for Cations

Molecule	$E_{1/2}$ vs. sce	$E$ , $\beta$ units	$10^9k$
Phenothiazine	0.59	0.129	6.7
Phenoxazine	0.59	0.270	4.5
10-Methylphenothiazine	0.73	0.312	2.2
Phenoxathiin	1.25	0.412	0.36

highest occupied orbital in units of  $\beta$  and the electrochemical half-wave potential. In Figure 3 the electron-transfer rate constants are plotted vs. these quantities. The HMO energies were calculated using the parameters employed by Bolton and Sullivan.<sup>49</sup> The electrode potentials for phenothiazine and 10-methylphenothiazine are given by Billon,<sup>24a</sup> that of phenoxathiin by Cauquis, *et al.*,<sup>50</sup> and the phenoxazine value was obtained in the course of this study.

The correlations are actually quite good and indicate that the energy required to remove the electron from the

(48) A. Streitweisser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.

(49) P. D. Sullivan and J. R. Bolton, *J. Magn. Resonance*, **1**, 356 (1969).

(50) C. Barry, G. Cauquis, and M. Maurey, *Bull. Soc. Chim. Fr.*, 2510 (1966).

(46) T. Kitagawa, T. Layloff, and R. N. Adams, *Anal. Chem.*, **36**, 925 (1964).

(47) J. Oakes and M. C. R. Symons, *Chem. Commun.*, 244 (1968).

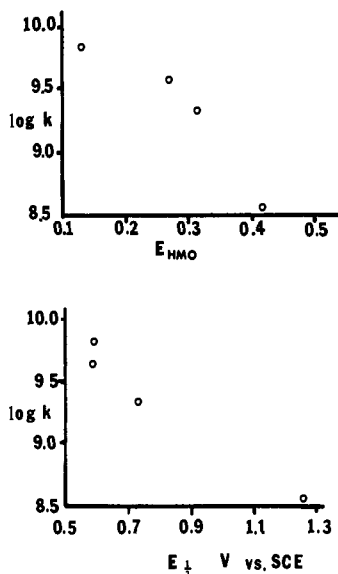


Figure 3. Molecular correlations for cations.

parent may play a key role in determining the electron-transfer rate constant for cation radicals. This is especially encouraging since this is the first systematic study of a series of cation radicals.

Correlation is also possible with ionization potentials and the agreement is again good also with the exception of Wurster's Blue. Bloor, *et al.*,<sup>51</sup> give the experimental ionization potential of Wurster's Blue cation to be 6.50 eV, which with its rate constant of  $1.0 \times 10^9$  does not correlate with the phenothiazine compounds. No data were available for the Wurster's Red cation. Since there is a major structural difference between the Wurster's salts and the phenothiazines, the use of a simple one-parameter correlation may not be adequate.

The picture is different for the substituted benzonitrile anions. Table V gives the HMO energies in

Table V. Molecular Correlations for Nitriles

Molecule	$-E_{1/2}$	$-E_{HMO}, \beta$ units	$10^{-9}k$
Benzonitrile	2.74 <sup>a</sup>	0.816	5.5
Phthalonitrile	2.12 <sup>a</sup>	0.723	12
Terephthalonitrile	1.97	0.694	14
Pyromellitonitrile	1.02 <sup>a</sup>	0.583	9.0
4-Cyanopyridine	2.03 <sup>a</sup>	0.667	6.8
4-Tolunitrile	2.75 <sup>a</sup>	0.806	7.8
3-Tolunitrile		0.814	5.6
2-Tolunitrile		0.810	8.6
Nitrobenzene	1.15 <sup>b</sup>	0.379	0.30 <sup>c</sup>
<i>p</i> -Chloronitrobenzene	1.06 <sup>b</sup>		0.79 <sup>c</sup>
<i>m</i> -Nitrobenzonitrile	0.94 <sup>b</sup>	0.378	1.6 <sup>c</sup>
<i>m</i> -Dinitrobenzene	0.90 <sup>b</sup>	0.345	5.2 <sup>c</sup>
<i>p</i> -Dinitrobenzene	0.69 <sup>b</sup>	0.200	6.0 <sup>c</sup>

<sup>a</sup> Determined *vs.* Ag|AgClO<sub>4</sub>. <sup>b</sup> Determined *vs.* sce. <sup>c</sup> Data taken from ref 4.

units of  $\beta$  of the lowest lying antibonding orbital and the reduction half-wave potentials. In Figure 4 these quantities are plotted *vs.* the electron-transfer rate constant. The reduction potentials are taken from Rieger, *et al.*,<sup>42</sup> while the HMO energies were either

(51) J. E. Bloor, B. R. Gilson, R. J. Haas, and C. L. Zinkle, *J. Mod. Chem.*, 13, 922 (1970).

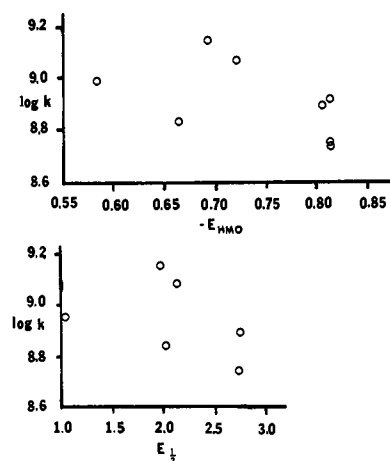


Figure 4. Molecular correlations for nitriles.

taken from Rieger and Fraenkel<sup>52</sup> or calculated with the parameters given there. These correlations are not as good as those for the cations; however, the range of rate constants is only a factor of 3 for these compounds.

It is possible to look for correlations among several of the nitrobenzene anions studied in DMF by Adams, *et al.*<sup>4</sup> Table V also gives the reduction potentials and the HMO energy of the lowest antibonding orbital for nitrobenzene, *p*-chloronitrobenzene, *m*-dinitrobenzene, *p*-dinitrobenzene, and *m*-nitrobenzonitrile. The HMO energies were calculated by Rieger and Fraenkel<sup>53</sup> while the reduction potentials were measured by Maki and Geske.<sup>54</sup> The correlation for reduction potential and rate constant is quite good while that for the HMO energies suffers by comparison. These are species where solvation is presumed to play an important role and it seems logical that the experimentally determined reduction potential should give a better fit than the HMO energy.

Molecular geometry can affect electron-transfer rates and this effect is quite striking for the electron transfer involving the cyclooctatetraene anion radical.<sup>55</sup> The electron transfer between the anion and dianion is quite rapid with a rate constant of about  $10^9$ , while that between the parent and anion is very much slower, the rate constant being  $10^5$  or less. The difference is attributed to the fact that the anion and dianion are planar while the parent is nonplanar.

There is some question as to the structures of the parents and cations of phenothiazine and the related compounds. In the case of phenothiazine Pullman and Malrieu<sup>56</sup> stated that both the parent and cation were folded along the axis passing through the nitrogen and sulfur atoms. Lhoste and Tonnard,<sup>24d</sup> however, appear to favor a planar radical, although they state that a definite conclusion is hard to reach. From dipole moment considerations Leonard and Sutton<sup>57</sup> concluded that the parent dihedral angle was 140–150°. Their measurements were made in benzene solution.

(52) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, 37, 2795 (1962).

(53) P. H. Rieger and G. K. Fraenkel, *ibid.*, 39, 609 (1963).

(54) A. H. Maki and D. H. Geske, *J. Amer. Chem. Soc.*, 83, 1852 (1961).

(55) T. J. Katz, *ibid.*, 82, 3785 (1960).

(56) J. P. Malrieu and B. Pullman, *Theor. Chim. Acta*, 2, 293 (1964).

(57) N. J. Leonard and L. E. Sutton, *J. Amer. Chem. Soc.*, 70, 1564 (1948).



Two studies of phenothiazine in charge-transfer complexes also have bearing on its geometry. An X-ray analysis by Fritchie<sup>58</sup> of the complex with 1,3,5-trinitrobenzene revealed it to be nonplanar with a dihedral angle of 165–172°. Bloor, *et al.*,<sup>51</sup> found good agreement between ionization potentials obtained from the charge-transfer complexes mentioned earlier and that calculated assuming a planar geometry using the Pariser–Pople–Parr method. Since phenothiazine is the electron donor in both complexes, its structure in the complex may be different from that of the parent and closer to that of the cation. The reason for Bloor's good agreement<sup>51</sup> could be that in the complex a planar or near-planar structure exists but this same structure might not be the case for the free molecule in solution.

The electron-transfer rate constant for phenothiazine is quite large,  $6.7 \times 10^9$ , which would seem to indicate that any difference between its structures, geometrically or energetically, is small. While 10-methylphenothiazine and phenoxazine have not been the subject of as much study, similar arguments would seem to apply since they too have fairly large rate constants. It should be noted that crystalline phenoxazine is planar.<sup>59</sup> This would not necessarily be so in the liquid phase but it would seem less distorted than the molecules containing sulfur atoms.<sup>59</sup> In fact, Bloor, *et al.*,<sup>51</sup> have shown that the dipole moment of phenoxazine can be explained in terms of a planar structure.

Phenoxathiin has a rate constant of only  $3 \times 10^8$ . The dihedral angle of 138° for the parent was measured by Le Fevre<sup>60</sup> and coworkers in benzene and carbon tetrachloride solutions. This is considerably more folded than phenothiazine and phenoxazine and the difference may result from a greater geometric differential between the parent and the radical.

The majority of radicals and parents studied here are polar; the electron-transfer reaction can then be characterized as taking place between dipolar species. It is also a reaction between an ion and a dipole. These two types of reaction have been discussed by several authors<sup>61,62</sup> and so only a brief summary is given now.

In a solution with macroscopic dielectric constant  $D$ , the potential energy between an ion and a dipole is given by

$$u = ze\mu \cos \theta / Dr^2 \quad (13)$$

where  $\mu$  is the permanent dipole moment,  $ze$  is the ionic charge, and the orientation of the ion and dipole is specified by



The direction of the dipole moment vector is from the partial positive to the partial negative charge. For an anion  $z$  is negative and the potential energy has its maximum attractive value when  $\theta = 0$ .

The potential energy for two dipoles in a solvent with macroscopic dielectric constant  $D$  is an attractive max-

(58) C. J. Fritchie, Jr., *J. Chem. Soc. A*, 1328 (1969).

(59) S. Hosoya, *Acta Crystallogr.*, 16, 310 (1963).

(60) M. J. Aroney, G. M. Hoskins, and R. J. W. Le Fevre, *J. Chem. Soc. B*, 960 (1969).

(61) E. A. Moelwyn-Hughes, "The Kinetics of Reactions in Solutions," Oxford Press, Clarendon, 1947.

(62) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960.

imum when the two dipoles are aligned head to tail and is given by

$$u = -2\mu_1\mu_2/Dr^3 \quad (14)$$

Regardless of whether a cation–dipole/parent–dipole or anion–dipole/parent–dipole pair is involved, the orientation for maximum attractive potential will be head–tail and is the sum of eq 13 and 14.

$$E = -\mu_1(e + 2\mu_2/r)/Dr^2 \quad (15)$$

For  $\mu_1 = \mu_2 = 4D$ ,  $r = 4 \text{ \AA}$ , and  $D = 35$ , the total interaction energy for the two terms gives an energy of about 1.0 kcal/mol, with the ion–dipole term accounting for about two-thirds of the total.

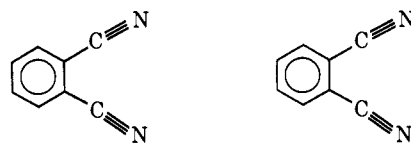
As a consequence of these interactions, the head–tail configuration for dipolar radicals and parents is assumed to give a preferred orientation for electron transfer. The dipole moment of benzonitrile,  $3.9D$ ,<sup>63</sup> is directed toward the nitrogen. This is also true of the toluenitriles because the dipole moment of toluene,  $0.37D$ ,<sup>63</sup> is much smaller than that of benzonitrile. For 4-cyanopyridine the total dipole moment likewise points out along the nitrile group. The dipole moment for phthalonitrile points out between the two nitrile groups.

The electron transfer then takes place between the nitrile group of the ion and the ring position of the parent to which it is directed by the dipole–dipole interaction. The logarithm of the rate constant is then assumed to be proportional to the sum of the spin densities on the nitrile group and the ring position.

The pertinent ring position for most of the parents is the position para with respect to the nitrile group, *i.e.*



The spin density at this position is usually the largest of the ring atoms except for the one to which the nitrile group is attached. The lineup for phthalonitrile, however, would be



with two nitrile groups assumed interacting with two ring positions.

This treatment was carried out assuming that only the nitrile nitrogen interacted with the ring and then both the carbon and nitrogen were included. Of the two the latter was the best and is shown in Figure 5.

The spin densities came from the work of Rieger and Fraenkel<sup>52</sup> or calculations made using their HMO parameters. Additionally, the rate constants for benzonitrile in the solvents acetonitrile, dimethyl sulfoxide, and propylene carbonate are included by multiplying the appropriate spin densities by the ratio of the dielectric constant of dimethylformamide to their dielectric constant. Rieger and Fraenkel<sup>52</sup> also give McLachlan spin densities but their use does not change the correlation. The total spin density at the interacting positions is about 20% higher, however.

(63) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill, New York, N. Y., 1955.

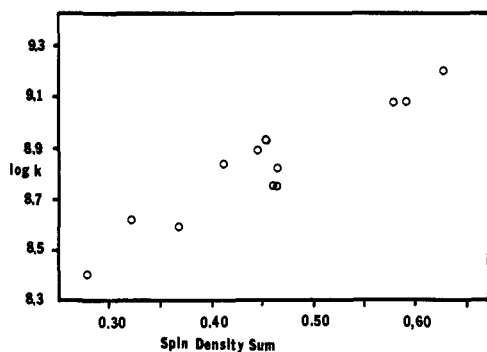
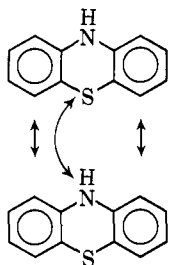


Figure 5. Dipolar correlation for nitriles using nitrile nitrogen and carbon.

The same type of correlation should apply to dibenzofuran, dibenzothiophene, and the 1,4-naphthoquinone anion studied by Adams.<sup>4</sup> These molecules were included in the correlation shown. The anions of terephthalonitrile and pyromellitonitrile were not included since their molecular dipole moments are zero. Nonetheless, it is interesting that a simple physical model gives an adequate correlation between electron-transfer rate constants and spin densities of atoms dictated by the model in systems where it is applicable.

The same dipolar model can also be used for the phenothiazine-like cation radicals. The lineup would be



but exactly which atoms are involved will depend on the geometry of the radical and parent. If geometric differences are small, all the atoms joined by arrows would be considered while if the geometric differences were large, only the heteroatoms would be important. The former gives better agreement, giving the correct order of rate constants and a straight line, except for 10-methylphenothiazine which is predicted to be as fast as phenothiazine. The latter predicts the order 10-methylphenothiazine > phenoxazine > phenothiazine > phenoxathiin.

For phenoxathiin approximately 90% of the spin density of interaction between the two molecules is contained on the sulfur and oxygen atoms<sup>58</sup> and if the difference in structure between parent and cation were the largest of the cations, the value for its large geometrical difference would still correlate well with that for the other molecules with small geometrical differences.

The approach used here suggests that the rate-controlling factor in electron transfer might not be "delocalization" as originally proposed by Adams.<sup>4</sup> In our case the pertinent spin densities are those of the parent and radical atoms nearest each other in the preferred orientation. These can be large without an "even" electron distribution which "delocalization" implies.

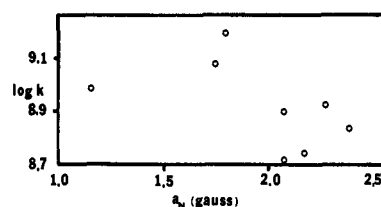


Figure 6. Nitrogen coupling constant correlation.

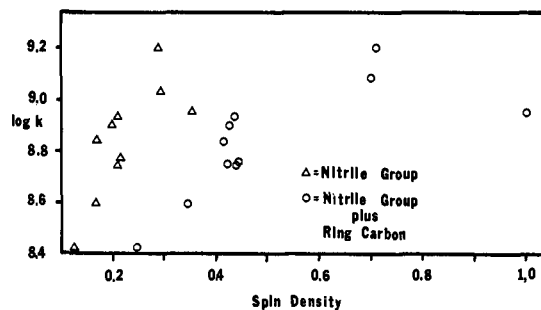


Figure 7. Intramolecular spin density correlations for nitriles using nitrile group and ring carbon.

However, the electron density at a given position has a better chance of being larger if the electron distribution is uniform. Additionally, using "localization" and/or "delocalization" as standards for the rates of electron-transfer reactions can be misleading. For example, in the solvated nitro anions the spin density on the nitro group is quite high and if the spin density there increases, a decrease in rate constant usually occurs. One cannot say that the slower electron-transfer rate takes place through the more tightly solvated nitro group since it is also possible that the electron transfer occurs from the ring, where the spin density has decreased.<sup>64</sup>

The above, however, should not be taken to mean that spin-density type correlations are not possible, and in fact in the following it will be seen that one may, with care, correlate these rates quite satisfactorily with spin densities.

Since the nitrogen hyperfine coupling constants in nitrobenzenes correlate nicely with electron-transfer rate constants, an analogous comparison of nitrile nitrogen coupling constants might appear to be in order. As demonstrated in Figure 6 the nitriles leave much to be desired. Had the solvent dependence been included as was done previously, more scatter would have been introduced. The reason for this failure is the nitrogen coupling constant is dominant in nitrobenzenes<sup>53</sup> but is not for the nitriles.<sup>42</sup> Even if the largest coupling constant for each nitrile is plotted *vs.*  $\log k$ , considerable scatter is present.

It should be realized that the nitrile nitrogen coupling constant depends on spin densities other than that of the nitrogen.<sup>52</sup> A more meaningful result and a better correlation is obtained if spin densities are correlated. Accordingly, in Figure 7 the spin densities for the nitrile group and the ring carbon to which it is attached and the nitrile group alone have been plotted. The agreement is definitely better than for the coupling

(64) L. S. Degtyarev, A. M. Golubenkova, and A. I. Brodskii, *Dokl. Phys. Chem.*, **191**, 217 (1970).

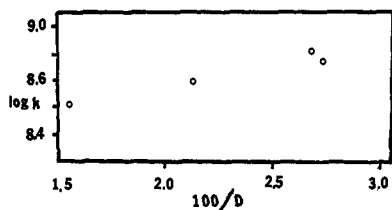


Figure 8. Dipolar treatment of solvent effect assuming a solvent-independent frequency factor.

constants and is comparable but not quite as good as that for the dipolar model.

Clearly several correlations are possible; however, the deeper meaning, if existent, will not become known until sufficient data are available to test the generality of each correlation.

**Solvent Effects.** The effects of solvent on electron-transfer reactions were also studied by varying the solvent for the benzonitrile anion radical. Dimethylformamide, acetonitrile, dimethyl sulfoxide, propylene carbonate, and dioxane were employed. The variation of the rate constant with solvent will be discussed using the simple ion-dipole, dipole-dipole theory introduced previously and with the more sophisticated theory due to Marcus.<sup>21,65,66</sup>

In the previous section, when correlating the rates in a single solvent the interaction energy due to the ion-dipole, dipole-dipole model was given by

$$E_d = -\mu(e + 2\mu/r)/Dr^2 \quad (16)$$

The rate constant for an electron-transfer reaction is assumed to be given by

$$k = Ae^{-(E_a + E_d/RT)} \quad (17)$$

where  $A$  is a frequency factor which is assumed for the present to be independent of solvent and  $E_a$  represents all other factors contributing to the activation energy. It is assumed independent of solvent. Equation 17 can be rewritten as

$$k = Ze^{-E_d/RT} \quad (18)$$

or

$$\ln k = \ln Z + \mu(e + 2\mu/r)/RTDr^2 \quad (19)$$

which predicts that the rate constant should decrease as the dielectric constant increases. This is exactly what has been observed for all solvents except dioxane. Dioxane has a dielectric constant of 2 and does not agree with this model, but with so low a dielectric constant ion pairing must certainly be more of a factor than for the other solvents. These results are shown plotted in Figure 8.

From the slope of the graph a value of  $r = 4 \text{ \AA}$  can be obtained for the distance between the ion-dipole or dipole-dipole. The dipole moment of the benzonitrile anion has been assumed equal to that of the parent ( $3.9D$ ).<sup>63</sup> This distance should probably not be taken too seriously but it does indicate that electron transfer is not a long-range process.

We have assumed that the solvent dependence of electron transfer is governed by  $E_d$  of eq 16. Accepting this, one can calculate the change in rate constant for

(65) R. A. Marcus, *Electrochim. Acta*, **13**, 995 (1968).

(66) R. A. Marcus, *J. Chem. Phys.*, **43**, 679 (1965).

a given anion going from one solvent to another. For example, when changing from dimethylformamide to propylene carbonate at room temperature the dielectric constant changes from 35 to 64. Assuming the separation to be  $4 \text{ \AA}$ ,  $E_d$  decreases by  $0.38 \text{ kcal/mol}$ . The change in activation energy predicted by eq 17 is  $0.41 \text{ kcal/mol}$ . The agreement is good but, once again, the simple nature of the model makes the agreement probably fortuitous.

The solvent independence of the frequency factor may seem questionable. For the benzonitrile systems, making it solvent dependent does not improve the agreement. The contribution to the activation energy from sources other than the dipolar energy will still be assumed to be solvent independent. The frequency factor is assumed to be given by<sup>62</sup>

$$A = 4\pi(r_A + r_B)(D_A + D_B)N/1000 \quad (20)$$

where  $N$  is Avagadro's number,  $r_A$  and  $r_B$  are the radii of the spherical molecules A and B, and  $D_A$  and  $D_B$  are the diffusion coefficients which are related to the viscosity by the Stokes-Einstein relation

$$D = kT/6\pi\eta r \quad (21)$$

The plot for a solvent-dependent frequency fraction is much more scattered than that shown in Figure 8.

It appears that the bulk dielectric constant of the solvent provides a means of correlating electron-transfer rates with solvent, provided the dielectric constant does not become too small.

One should realize, however, that in the fast exchange limit appreciable amounts of benzonitrile are present. Because of its density ( $0.996 \text{ g/cm}^3$ ) and molecular weight (103) a  $1.0 M$  solution of benzonitrile is about 10% benzonitrile by volume. All but two of the forty samples of benzonitrile studied in the various solvents were  $5 M$  or higher, meaning the benzonitrile content of the samples was usually less than 50% and more than 10% by volume.

The dielectric constants of all the solvents except dioxane are greater than that of benzonitrile (25.6). Since the solvation energy for an ion in solution increases as the dielectric constant increases, this could mean that even though as much benzonitrile as solvent is present in solution, the benzonitrile anion is solvated by the solvent which mediates the electron transfer. The close distance of parent radical approach,  $4 \text{ \AA}$ , obtained earlier would seem to leave room for little more than one solvent molecule at most between the ion and parent. As mentioned previously, that distance should probably not be taken too seriously. It should be noted that an attempt to include the dioxane rate constant by using the benzonitrile dielectric constant instead of that of dioxane does not work since the benzonitrile dielectric constant (25.6) would predict a rate constant larger than the one observed in dimethylformamide and acetonitrile.

An examination of the frequency factors calculated here, which should be the approximate diffusion-controlled rate constants for these solvents, shows that none of the anions studied in dimethylformamide are near diffusion control with the same holding true for the cations in acetonitrile. Phenothiazine comes the closest, being slower than the limit by a factor of 3.

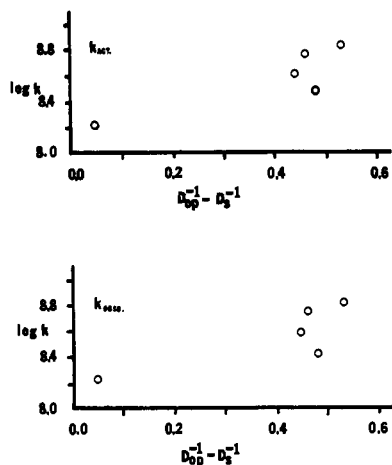


Figure 9. Plot of rate constants *vs.* Marcus dielectric parameter.

The variation of rate constant with solvent can also be used to test the theory of Marcus.<sup>21,65,66</sup> In this theory the rate constant for an activation-controlled electron-transfer reaction is

$$k_{\text{act.}} = Z e^{-\Delta F^*/RT} \quad (22)$$

where  $\Delta F^*$  is the free energy of activation and  $Z$  is a collision number of about  $10^{11}$  l./mol sec). The free energy of activation is given by

$$\Delta F^* = \frac{\omega^r + \omega^p}{2} + \frac{\lambda}{4} + \frac{\Delta F^\circ}{2} + \frac{(\Delta F^\circ + \omega^p - \omega^r)^2}{4\lambda} \quad (23)$$

where  $\Delta F^\circ$  is the standard free energy of reaction,  $\omega^r$  and  $\omega^p$  are the work necessary to bring together the reactants and products in the activated complex, and  $\lambda$  is the solvent reorganization parameter, which is given by

$$\lambda = \left( \frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r} \right) \left( \frac{1}{D_{\text{op}}} - \frac{1}{D_s} \right) (\Delta e)^2 \quad (24)$$

The effective radii of the reactants are  $a_1$  and  $a_2$ ,  $r$  is  $a_1 + a_2$ ,  $\Delta e$  is the difference in charge between the reactants,  $D_{\text{op}}$  is the optical dielectric constant of the solvent, which is the square of its refractive index, and  $D_s$  is the static dielectric constant.

For the type of electron-transfer reactions we have studied, the standard free energy of reaction is zero and the work terms are small, since one of the reactants is the neutral parent. Even if some model such as the ion-dipole or dipole-dipole interactions were used this would still be small compared to the term involving  $\lambda$ . A plot of  $k$  *vs.*  $\lambda$  should then yield a straight line.

If the rate constant is near the diffusion-controlled limit, the experimentally observed rate constant is related to that for activation controlled and diffusion controlled by<sup>67</sup>

$$k^{-1}_{\text{obsd}} = k^{-1}_{\text{diff}} + k^{-1}_{\text{act.}} \quad (25)$$

and the diffusion-controlled term must be taken into account before a comparison of theory and experiment

(67) R. A. Marcus, *Discuss. Faraday Soc.*, **29**, 129 (1960).

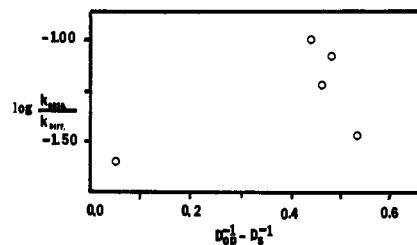


Figure 10. Plot of rate constant *vs.* Marcus dielectric parameter assuming the frequency factor is solvent dependent.

for the activation-controlled term can be made. In Table VI the dielectric parameter  $D_{\text{op}}^{-1} - D_s^{-1}$  and

Table VI. Observed Rate Constant Corrected for Diffusion Control and Dielectric Parameter

Solvent	$10^{-8}k_{\text{obsd}}$	$10^{-9}k_{\text{diff}}$	$10^{-8}k_{\text{act.}}$	$D_{\text{op}}^{-1} - D_s^{-1}$
Dimethylformamide	5.5	9.4	5.8	0.46
Acetonitrile	6.6	20	6.8	0.53
Dimethyl sulfoxide	3.8	3.7	4.2	0.44
Propylene carbonate	2.6	3.1	2.8	0.48
Dioxane	1.7	6.8	1.8	0.48

the various rate constants are given. In Figure 9 both  $k_{\text{obsd}}$  and  $k_{\text{act.}}$  are plotted *vs.* the dielectric parameter.

The agreement is not good. In fact the trend is the reverse of what might be expected. As  $D_{\text{op}}^{-1} - D_s^{-1}$  decreases, the rate constant is predicted to increase but our data show a decrease as the parameter decreases.

The agreement can be improved by making the frequency factor  $Z$  solvent dependent. This is contrary to the Marcus theory but is included since the correlation is considerably better than the other two. In Figure 10  $\log k_{\text{obsd}} - \log k_{\text{diff}}$  is plotted *vs.*  $D_{\text{op}}^{-1} - D_s^{-1}$  and the improved agreement can be readily seen. If a straight line is drawn through the four points excluding dioxane, the slope can be used to determine the radius of the reactant, assuming  $a_1 = a_2 = a$ . At room temperature the slope is about  $-7$  and a distance of  $r = a$  of  $4.4 \text{ \AA}$  is obtained. This means the separation of the radical and parent in the activated complex is about  $9 \text{ \AA}$ , which is larger than the separation obtained for the dipolar model.

It would appear that Marcus theory as originally postulated does not give adequate agreement with experiment and that additional parameters need to be introduced to obtain agreement considering only our data. However, if it is considered with the results of other determinations of electron-transfer rate constants, the introduction of a solvent-dependent frequency factor is unnecessary.

Brandon and Dorfman<sup>68</sup> studied the electron-transfer reaction between the pyrene anion radical and 9,10-dimethylanthracene using pulse radiolysis techniques in the solvents diethylamine, ethylenediamine, 2-propanol,

(68) L. M. Dorfman and J. R. Brandon, *J. Chem. Phys.*, **53**, 3849 (1970).

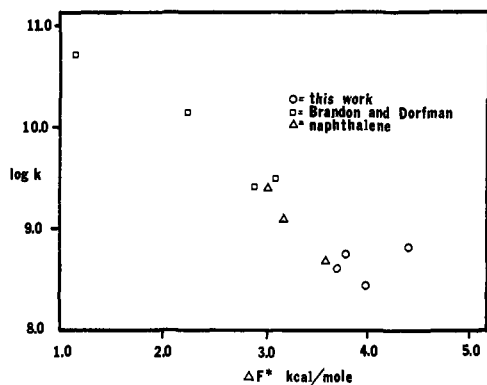


Figure 11. Plot of rate constant vs. Marcus free energy for several electron-transfer reactions.

and ethanol. Their work is different from ours in several respects.

The electron-transfer reaction between benzonitrile and its anion radical has a standard free energy of zero since the reactants and products are identical. This is not the case for the cross reaction they studied which has a standard free energy of activation of  $-2.01$  kcal/mol. This nonzero free energy as well as the solvation term involving the dielectric constant and index of refraction contributes to the free energy of

activation. Figure 11 plots  $\log k$  vs.  $\Delta F^*$  for their data and ours.

It should be noted that one of their solvents, diethylamine, has a dielectric constant of 3.8 but fits the correlation. This is because their solutions contain only reactants and solvents; there is no supporting electrolyte present to take part in ion pairing. Also included in Figure 11 are three points for the electron-transfer reaction between the naphthalene free anion radical and its parent determined by esr. The information is taken from Table V of the work of Szwarc, *et al.*,<sup>69</sup> where references to the original literature are given.

As can be seen in Figure 11 the overall agreement is quite good and the Marcus theory appears to give a reasonable description of the electron-transfer reactions of this group of organic radicals where ion pairing is not thought to play a significant role.

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## Electron Paramagnetic Resonance Studies of Triple Ions and Alcohol-Solvated Ion Pairs of Anthraquinone<sup>1</sup>

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**Abstract:** Comprehensive epr studies of triple ions ( $M^+A^-M^+$ ) and alcohol-solvated ion pairs ( $M^+A^-HOR$ ) of anthraquinone are reported. The process of the formation of Li, Na, and K triple ions and the kinetics of the formation and dissociation of triple ions were studied. The role of triple ion formation in the intermolecular cation-transfer reaction was clarified. The structures of triple ions and the spin distributions in triple ions are studied and compared with those of ion pairs. The improved MO calculations of the spin distributions in ion pairs and triple ions are reported. The structures of solvated ion pairs were determined from the direction of the changes of spin densities upon solvation. The changes of alkali metal splittings upon solvation were also studied and discussed in terms of the structures of solvated ion pairs and triple ions.

The presence of triple ion,  $R^-(M^+)_2$ , and ion quadruplet,  $R^-(M^+)_2X^-$ , in dilute ethereal solutions of radical ions having two polar groups in symmetric positions has been reported on several occasions.<sup>2-7</sup> The structures of such species<sup>3,5-7</sup> and the possible

roles of these species in intermolecular cation-transfer reactions<sup>4,8-10</sup> have been discussed recently. However, the properties of the triple ions and ion quadruplets have been investigated far less than those of ion pairs,  $R^-M^+$ , and there are many unknown aspects about their structural and kinetic properties. Their kinetic properties, in particular, are not yet well understood.

The present paper describes our attempts to obtain a comprehensive understanding of the properties of triple ions and ion quadruplets. We first investigated the

(1) This research was supported by the grant from the National Science Foundation.

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