Determination of Electron Transfer Rate Constants in Solutions of Benzene, Toluene, and p-Xylene Radical Anions Using Electron Spin Resonance Spectroscopy and Computer Simulation Techniques

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Abstract: The rates of electron transfer between radical anions and their neutral molecules for the benzene, toluene, and p-xylene systems have been extensively investigated in order to obtain information concerning the effects of ethereal solvents, cations, and substituent upon the rate of electron transfer. The esr spectra for these systems were simulated using Piette and Anderson's total line shape expression rearranged to a form particularly suitable for computer calculation. Comparison between experimentally observed spectra and computed spectra made it possible to calculate the rate constants, not only in the fast exchange regions, but also in the intermediate regions of exchange. The rate constants and apparent energies of activation were found to be small and large, respectively, for each compound investigated relative to other previously investigated anion systems. Also, the rate constants for these systems show systematic variations as the neutral molecule concentration increases. Solvent and structural effects on the rates were also observed.

In recent years there has been considerable interest in the determination of electron transfer rates using the techniques of electron spin resonance (esr) spectroscopy.[2–12] The rate constants have been calculated in either the exchange-broadened limit where the spectral lines, although broadened, are still well resolved, or in the fast, or exchange-narrowed limit, where two or more lines have been collapsed into one sharp Lorentzian line. For example, Ward and Weissman[2a] utilized the exchange-broadened limit in their study of the naphthalenide–naphthalene electron-transfer reaction. The appropriate formula for calculation of the rate constant in the limit of small broadenings ($|w_i - w_j|\tau \gg 1$), assuming Lorentzian lines shapes, is

$$k = \frac{1.52 \times 10^7 \Delta H}{C} \quad (1)$$

where ΔH is the peak-to-peak increase in line width in gauss due to exchange, for the derivative curve, and C is the concentration of neutral material (diamagnetic form) in moles/liter. Chang and Johnson[9] examined the same systems and calculated the rate constants from exchange-narrowed spectra using the simple formula

$$k = \frac{2.03 \times 10^7 \nabla}{\Delta H(C)} \quad (2)$$

where ∇ is the second moment in (gauss)² for the unbroadened spectrum in the absence of chemical exchange, ΔH is the peak-to-peak line width of the derivative curve corrected for natural line width, in gauss, and C is the concentration of neutral material (diamagnetic form) in moles/liter. This expression is derived by applying the limiting condition $|w_i - w_j|\tau \ll 1$ to the full line shape function for an N-site exchanging system.[13] However, direct determination of the rate of electron transfer in the intermediate regions of exchange has not been carried out.

In this paper the rate constant for electron exchange between a free radical and its neutral precursor (benzene, toluene, and p-xylene systems) is calculated not only in the fast exchange region, but also in the intermediate regions of exchange.

The initial theoretical treatment of an N-site exchanging system in which the magnetization is transferred from site j to any of the N sites on another molecule is due to Piette and Anderson.[13] These authors, using the approach of Gutowsky, *et al.*,[14] to the Bloch equations, obtained an expression for the total transverse magnetization, which is outlined below, and showed that it reduces to simple forms in the limits of slow and fast exchange. (Much of the early theoretical work has been reviewed by Johnson.[15]) More recently Allerhand and Thiele[16] and Hoffman[17] have examined similar effects in connection with Carr–Purcell spin-echo trains. With application directly to electron-transfer reactions as studied by esr in mind, Norris[18] has presented a derivation of Piette and Anderson's expression, rearranged to a form particularly suitable for

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(2) (a) R. L. Ward and S. I. Weissman, *J. Amer. Chem. Soc.*, **79**, 2086 (1957); (b) W. D. Phillips, J. C. Rowell, and S. I. Weissman, *J. Chem. Phys.*, **33**, 626 (1960).

(3) P. J. Zandstra and S. I. Weissman, *J. Amer. Chem. Soc.*, **84**, 4408 (1962).

(4) M. T. Jones and S. I. Weissman, *ibid.*, **84**, 4269 (1962).

(5) W. L. Reynolds, *J. Phys. Chem.*, **67**, 2866 (1963).

(6) N. Hirota and S. I. Weissman, *J. Amer. Chem. Soc.*, **86**, 2537 (1964).

(7) T. Layloff, T. Miller, R. N. Adams, E. Fok, A. Horsfield, and F. Proctor, *Nature*, **205**, 382 (1965).

(8) W. H. Bruning and S. I. Weissman, *J. Amer. Chem. Soc.*, **88**, 373 (1966).

(9) R. Chang and C. S. Johnson, Jr., *ibid.*, **88**, 2338 (1966).

(10) G. L. Malinoski and W. H. Bruning, *ibid.*, **89**, 5063 (1967).

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

(12) R. Chang and S. I. Weissman, *J. Amer. Chem. Soc.*, **89**, 5968 (1967).

(13) L. H. Piette and W. A. Anderson, *J. Chem. Phys.*, **30**, 899 (1959).

(14) H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *ibid.*, **21**, 279 (1953).

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

(16) A. Allerhand and E. Thiele, *J. Chem. Phys.*, **45**, 902 (1966).

(17) R. A. Hoffman, *ibid.*, **46**, 3277 (1966).

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

computer calculations (see also the work of Alexander[19]). Utilization of computer line shape simulations makes possible experimental measurements in not only the slow and fast exchange limits, but also in the intermediate region of exchange rates. It is upon Norris' work that the calculations presented herein are based.

Theory

The Bloch equation describing the transverse magnetization of the jth site undergoing exchange with N other sites may be written as

$$\left(\frac{d}{dt} + \alpha_j\right)M_j{}^+ = iw_1M_{0j} + \sum_{k \neq j}^{N}\left[\frac{M_k{}^+}{\tau_{kj}} - \frac{M_j{}^+}{\tau_{jk}}\right] \quad (3)$$

where $M_j{}^+ = M_{xj} + iM_{yj}$, τ_{kj}, and τ_{jk} are the lifetimes for transfer from k to j and vice versa, respectively, w_1 is the frequency of the rf field, M_{0j} is the equilibrium magnetization of site j, and

$$\alpha_j = \frac{1}{T_{2j}{}^0} + i\Delta w_j \quad (4)$$

where $T_{2j}{}^0$ allows for the natural line widths. The sums on the right of (3) account for all transfer of magnetization into and out of j. Imposing the restriction that $\tau_{jk} = \tau_{kj} = \tau$, (3) becomes

$$\left(\frac{d}{dt} + \alpha_j\right)M_j{}^+ = iw_1M_0P_j +$$

$$\frac{1}{\tau}P_j\sum_k M_k{}^+ - \frac{1}{\tau}M_j{}^+\sum_k P_k \quad (5)$$

where P_k represents the fractional population of the kth site. Since (5) represents the magnetization of one site, we must sum over all N sites to obtain the total magnetization. Setting the time derivative to zero, solving for $M_j{}^+$, and performing the summation we find

$$M_{\text{total}}{}^+ = iw_1M_0 \frac{\displaystyle\sum_k^N \frac{P_k}{(1/T_{2k} + 1/\tau) + i(w_k - w)}}{1 - \frac{1}{\tau}\displaystyle\sum_k^N \frac{P_k}{(1/T_{2k} + 1/\tau) + i(w_k - w)}} \quad (6)$$

the imaginary part yielding the absorption line shape.

As Norris[18] has pointed out, (6) is quite easily solved numerically by a computer using the complex arithmetic functions available with FORTRAN IV,[20] the advantage over Piette and Anderson's original expression being that only one, instead of two sums need be calculated. For exchange rates which approach the fast-exchange limit, i.e., when the spectrum is collapsed to a single line, we have found it convenient to calculate the line widths corresponding to a number of different lifetimes, τ, and using these data prepare a plot of the line width vs. the lifetime. For a given experimental line width, one may then extrapolate a lifetime and determine the reaction rate. For slower rates, in which the spectrum retains some hyperfine structure, the width of some central component or the splitting distance between it and one of the outer components may be used as the parameter for determining the rate. (In the case of benzene we used the splitting of the $M_z = \pm 1$ lines of the spectrum in the intermediate exchange region.) Input for the computer program consists of coupling

constants, multiplicities, natural line widths, and τ values. Results of calculations performed on the naphthalene and stilbene free radical anion systems, in the strongly exchange-narrowed limit, studied by Chang and Johnson[9,11] are presented in Table I to illustrate the

Table I[a]

System	Computer rate constant[b] ($k \times 10^{-9}$ M^{-1} sec^{-1})	Second moment rate constant[c] ($k \times 10^{-9}$ M^{-1} sec^{-1})
Naphthalene[d,e]		
Na-DME	1.6 ± 0.1	1.6 ± 0.2
Na-THF	2.8 ± 0.3	2 ± 1.5
K-DME	2.0 ± 0.1	2.2 ± 0.4
K-THF	2.9 ± 0.1	3.0 ± 0.5
Stilbene[f]		
Na-DME	1.7 ± 0.1	1.8 ± 0.1

[a] We thank Drs. Chang and Johnson for allowing us use of their data. [b] "Full" line shape function. See Discussion section. [c] Equation 2. [d] 23°. [e] In all cases, if two superimposed lines occurred in the spectrum, the calculations were performed for the sharp line. [f] 16°.

agreement between computer and "second moment" values of the rate constants, for very sharp lines. (See Discussion below.)

Experimental Section

A. **Materials.** All aromatic compounds used (benzene, toluene, and p-xylene) as well as 1,2-dimethoxyethane (DME) and tetrahydrofuran (THF) solvents were commercially obtained. The solvents were fractionated, and a constant boiling middle fraction was collected. The aromatic compounds and solvents were vigorously refluxed for 24 hr over sodium/potassium alloy in a vacuum bottle equipped with a reflux condenser.[21] The compounds were then refluxed slowly under vacuum for many days by using an infrared heating lamp until use.

The alkali metals were purified and stored in capillary tubes according to the usual procedures.[22]

B. **Preparation of Anions for Rate Studies.** Each negative ion solution for a rate experiment was prepared in a Pyrex apparatus using the usual techniques (see ref 21).

Neutral aromatic concentrations were measured by vapor phase chromatography (vpc).[21] This was accomplished by obtaining unknown solvent to aromatic peak ratios via vpc recorder traces and comparing with a standard curve. All area ratios were based upon six vpc traces and, before an unknown concentration was to be determined, a standard solution was run through the vpc instrument, in order to check the standard curve.

C. **Esr Spectrometer.** All esr measurements described in the paper were made with a Jeolco-3BSX spectrometer operating near 9.7 kMHz, with linear field sweep and 100-kHz field modulation. Temperature was maintained and controlled with a Jeolco JES-UCT-2X variable temperature adapter on the esr cavity. The temperatures were measured with a copper–constantan thermocouple inserted below the sample. Temperature readings were quite constant if all settings were properly adjusted and were easily controlled to within $\pm 1°$.

Calibration of the field sweep was achieved either by the well-known 13.07-G splitting of peroxylamine disulfonate or with an nmr proton marker.

D. **Spin Counts.** The number of spins in a given sample was determined by comparing the area of its esr spectrum with the area of a standard sample esr spectrum at the same temperature (usually 18°). The standard sample was a weighed amount of recrystallized 1,1-diphenyl-2-picrylhydrazyl (DPPH)[23] dissolved in the same solvent as the sample whose spin concentration was to be determined, so that both samples would introduce into the esr microwave cavity approximately the same amount of "lossy" material.

(19) S. Alexander, *J. Chem. Phys.*, 37, 967, 974 (1962).
(20) Since the complex part of eq 6 can be extracted, use of complex arithmetic is not absolutely necessary: J. Norris, private communication.

(21) G. L. Malinoski, Jr., Ph.D. Thesis, University of Nebraska, 1969.
(22) D. E. Paul, Ph.D. Thesis, Washington University, 1954.
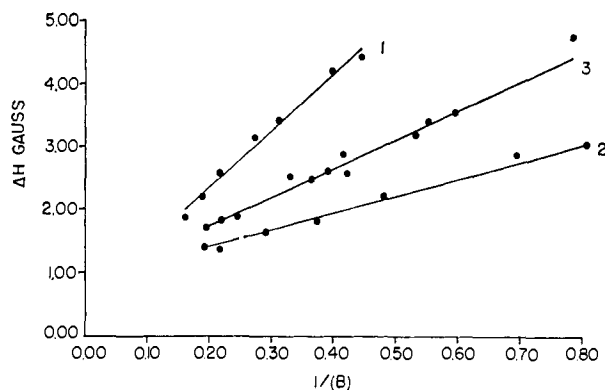(23) J. A. Weil and J. K. Anderson, *J. Chem. Soc.*, 5567 (1965).

Figure 1. Least-squares plots of line width $vs.$ reciprocal of benzene concentration in moles per liter: (1) K, DME, 18°; intercept = 0.54 G; (2) K, THF, 18°, intercept = 0.87 G; (3) Na/K alloy, THF-DME (2:1 ratio), 18°, intercept = 0.82 G.
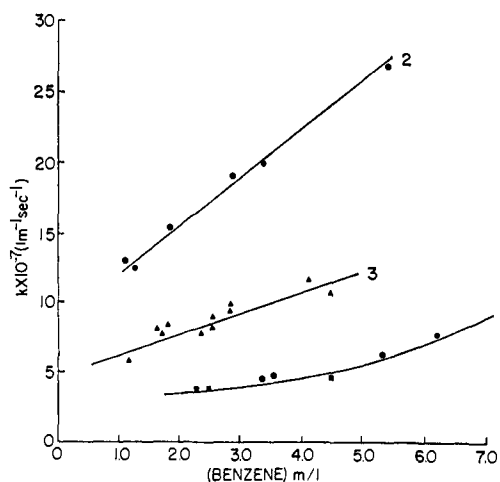

Figure 2. Dependence of rate constant for benzene-benzene anion system upon neutral benzene concentration: (1) K, DME, 18°; (2) K, THF, 18°; (3) Na/K alloy, THF-DME (2:1 ratio), 18°.

It was found for all systems investigated that the concentration of paramagnetic species could never be generated above 10^{-3} mol/l. The spectra used for this paper for determining rate constants and apparent energies of activation were taken in the concentration region of 10^{-4}–10^{-5} mol/l. of anion.

Results

A. **Line Shape Comparison.** The line shapes of the various systems were checked by comparing the collapsed first derivative line shape of an experimental spectrum with the derivative line shape of a theoretical spectrum simulated in the fast-exchange region. In all cases when hyperfine structure was absent correct choice of lifetime yielded simulated spectra which could be superimposed on the experimental spectra. Plots of peak-to-peak derivative curve width $vs.$ lifetime were constructed for each system and were used as working curves to determine the experimental lifetimes.

B. **Benzene Systems.** In order to calculate the rate of electron transfer by computer simulation, one needs to know the effective natural line width and coupling constants at a specific temperature for the particular system under investigation. To obtain this information, a series of experiments to investigate the temperature dependency of the effective natural line width and proton hyperfine coupling constant of the $C_6H_6^{-1}$ systems was performed.
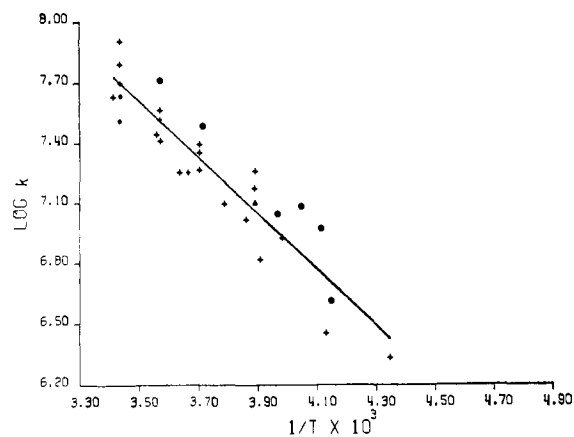

Figure 3. Least-squares activation energy plot for benzene reduced by K-DME.
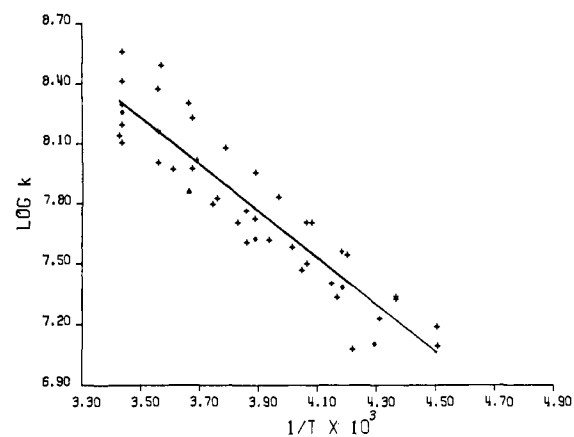

Figure 4. Least-squares activation energy plot for benzene reduced by K-THF.

The results in dilute solutions for coupling constant[24–26] and line width variation[27,28] with temperature agreed well with earlier studies. Also, we could detect no statistical difference between mixed solvent-Na/K alloy systems and systems prepared with pure solvents and a single metal. In all benzene computer simulations the effective natural line width used was obtained at each temperature from a plot of line width, in the absence of exchange, $vs.$ temperature.

An examination of Figures 1–5 for the various benzene systems indicates that there are significant differences in the apparent rate constants for the electron-transfer reaction and activation energies, as well as an apparent dependence of rate constant on the neutral benzene concentration at any specific temperature.

The plots of the total line width $vs.$ the inverse of the neutral benzene concentration (Figure 1) exhibit the expected linearity. The intercept of the various lines for systems at 18° are found in Table II. These intercepts approximate the effective natural line width in the absence of chemical exchange for each of these systems.

(24) R. G. Kooser, Ph.D. Thesis, Cornell University, 1968.
(25) G. L. Malinoski, Jr., and W. H. Bruning, $J.$ $Chem.$ $Phys.$, 50, 3637 (1969).
(26) R. G. Kooser, W. V. Volland, and J. H. Freed, $ibid.$, 50, 5243 (1969).
(27) R. W. Fessenden and S. Ogawa, $J.$ $Amer.$ $Chem.$ $Soc.$, 86, 3591 (1964).
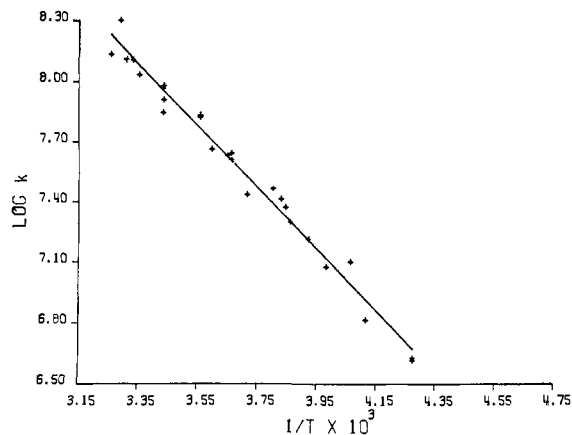(28) M. T. Jones, $ibid.$, 88, 174 (1966).

Figure 5. Least-squares activation plot for benzene reduced by Na/K alloy–THF–DME.

Figure 6. Plots of line width *vs.* reciprocal of concentration in moles per liter: (1) toluene, K, DME, 0°, intercept = 0.27 G; (2) *p*-xylene, K, DME, 18°, intercept = −0.11 G.

We were unable to satisfactorily correct the exchange-collapsed spectra for contributions to the width due to Heisenberg spin exchange broadening processes. Results of Miller and Adams[29] on Heisenberg spin exchange contributions to the line width in other hydrocarbon anion systems lead us to believe that any correction to exchange-narrowed line width in our experiments should be negligible.

Table II. Intercepts for Lines of Figure 1[a]

System	Intercept, G
K, DME	0.54 ± 0.10
K, THF	0.87 ± 0.10
Alloy, THF–DME	0.82 ± 0.20

[a] Temperature, 18°.

Uncertainty in experimentally obtaining the true effective natural line width for these three benzene systems, errors in measuring experimental line widths and neutral aromatic concentrations, and possible Heisenberg spin exchange contributions lead us to estimate the combined error in determination of the rate constant as ±25% at 18°. (A complete discussion of the method used to choose the natural line width for simulations, as well as a discussion of errors can be found in ref 21.)

The apparent activation energies and rate constants for the electron-transfer reaction studied in the present investigation are summarized in Table III. The rate

Table III. Rate Constants and Activation Energies for Benzene[a]

System	[Benzene], M	$k \times 10^{-7}$, $M^{-1} \sec^{-1}$	$E_A{}^{\ddagger}$, kcal
K, DME	2.24	3.6 ± 0.6	6.4 ± 1.0
Alloy, THF–DME	2.57	8.7 ± 1.3	7.0 ± 1.0
K, THF	2.08	16.3 ± 2.4	5.3 ± 0.8

[a] Temperature, 18°.

constants in Table III were selected, as nearly as possible at the same concentration. Other sets of rate constants could be singled out at different concentrations from Figure 2. Our purpose is to point out the relative

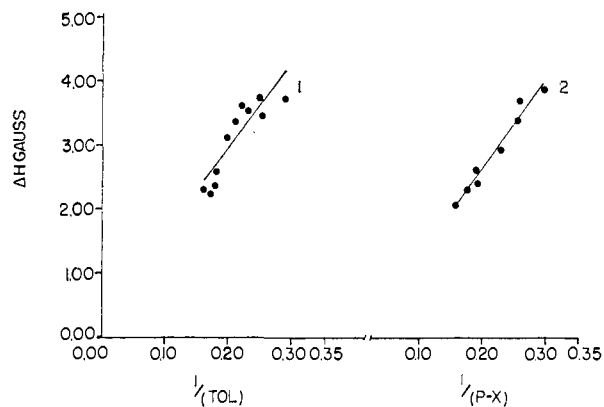(29) T. A. Miller and R. N. Adams, *J. Amer. Chem. Soc.*, **88**, 5713 (1966).

differences between particular cation–solvent systems at some nearly equivalent neutral benzene concentration, to illustrate the variation in rate constant.

C. **Toluene and *p*-Xylene Systems.** The proton coupling constants for toluene and *p*-xylene were taken from previous investigations.[30,31] Since we could not experimentally follow the temperature dependence of the line width and hyperfine coupling constants, if any, we assumed that these parameters were temperature independent. The effective natural line widths used in computer simulation of the toluene and *p*-xylene systems were 0.15 and 0.35 G, respectively. These values were arrived at by comparison with experimental spectra in the intermediate region of exchange. Spectra were simulated with various line widths until a set was obtained in this intermediate region that faithfully reproduced the experimentally observed collapse of the hyperfine structure as the lifetime was changed.[21] A curve of lifetime *vs.* exchange-narrowed line width was then calculated, exactly as in the case of the benzene systems previously discussed, and we were able to then calculate the rate constants in both the fast-exchange limit and the intermediate region of large broadening.

The plots of the total line width *vs.* the inverse of the neutral toluene or *p*-xylene concentration (Figure 6) exhibit the expected linearity. The intercepts for these systems are 0.28 ± 0.28 G for (K, DME), toluene at 0°, and −0.11 ± 0.12 G for (K, DME), *p*-xylene at 18°.

The narrow concentration range over which these plots were constructed may account for the discrepancy between the extrapolated value of the intercepts and the values used in computer simulation (also, see Discussion section below).

Assuming that the effective natural line width and coupling constants were independent of temperature, and considering the errors in measuring experimental line widths and possible spin-exchange broadening contributions, we estimate that the combined error involved in determining the rate constants due to these factors is of the order of ±10% between 0 and 18°.

Figure 7 indicates there is a functional dependence between the rate constant and neutral aromatic hydrocarbon concentration.

(30) J. R. Bolton and A. Carrington, *Mol. Phys.*, **4**, 497 (1961).
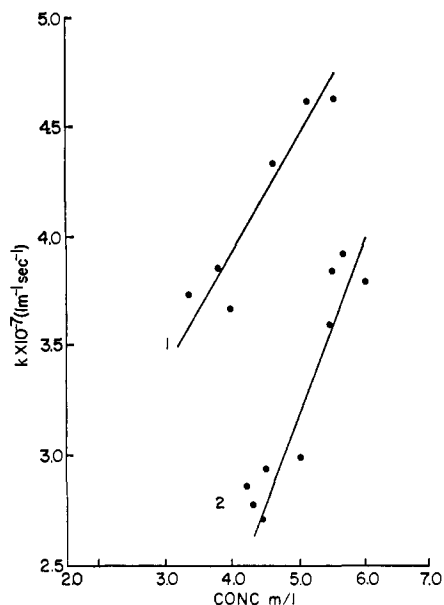(31) E. de Boer and C. MacLean, *J. Chem. Phys.*, **44**, 1334 (1966).

Figure 7. Dependence of rate constant upon neutral molecule concentration: (1) toluene, K, DME, 0°; (2) p-xylene, K, DME, 18°.
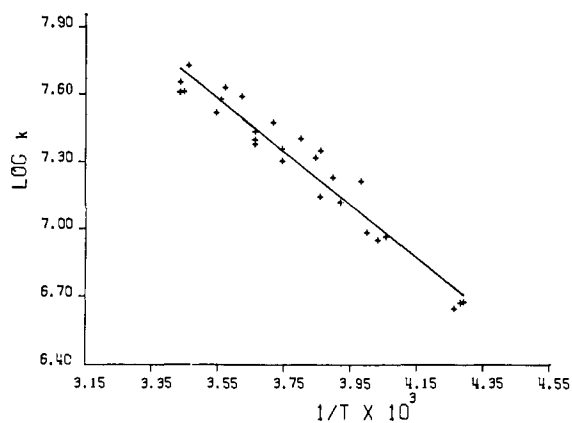

Figure 8. Least-squares activation energy plot for toluene reduced by K-DME.

Figure 9. Least-squares activation energy plot for toluene reduced by alloy-THF-DME.
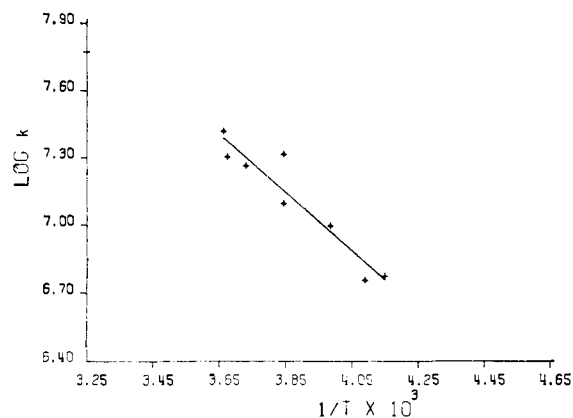
Figure 10. Least-squares activation energy plot for p-xylene reduced by K-DME.

The apparent activation energies and rate constants for the electron-transfer reactions of toluene and p-xylene are summarized in Table IV (Figures 6–10).

Table IV. Rate Constants and Activation Energies for Toluene and p-Xylene[a]

System	Concn, M	$k \times 10^{-7}$, M^{-1} sec^{-1}	$E_A{}^{\pm}$, kcal
(K, DME) toluene	4.77	4.5 ± 0.4	5.4 ± 0.4
(Alloy, THF–DME) toluene	5.29	6.6 ± 0.6	4.8 ± 0.4
(K, DME) p-xylene	4.77	4.3 ± 0.4	5.9 ± 0.6

[a] Temperature, 18°.

Again, we have tried to compare rate constants at the same concentration because of the dependence of rate constant on neutral aromatic molecule concentrations. The value for toluene with alloy reduction and 2:1 TMF–DME is at considerably higher neutral concen-
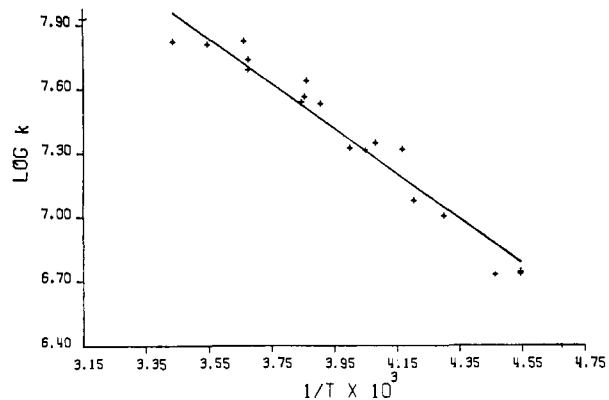
tration than the other two systems mentioned in the table. We were unable to study this system below 5.2 M neutral toluene at 18° because of radical stability problems.

Our results for p-xylene can be compared with the results obtained by de Boer and MacLean.[31] They studied this system with nmr techniques in the region of small broadenings and knew for certain they were dealing with an ion-paired species. They found the rate constant could be expressed as $k = 10^{12.0}$ exp $(-6200/RT)$ 1. mol^{-1} sec^{-1} for the K, DME system (activation energy in calories). Calculation of k at 18° using their expression yields $k = 2.3 \times 10^7$ 1. mol^{-1} sec^{-1}. Extrapolation of the curve in Figure 7 of this work to zero concentration dependence yields $k = 1.9 \times 10^7$ 1. mol^{-1} sec^{-1} at 18°. Our value for the apparent energy of activation is 5.9 ± 0.6 kcal. Assuming the validity of a linear extrapolation of the line in Figure 7, this agreement is reasonable. (This comparison assumes that the mechanism of the p-xylene–p-xylenide exchange reaction is essentially the same over the temperature range −86 to 18°.)

Discussion

A. Benzene Systems. Figure 2 indicates the functional dependence between the rate constants and neutral benzene concentration previously noted. One explanation for this effect might be the change in the bulk dielectric constant of the medium as the neutral

Table V

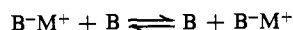| Pure compound	Dielectric constant[a]
THF	7.20[b]
DME	7.39[b]
Benzene	2.28[c]
Toluene	2.38[b]
p-Xylene	2.27[c]

[a] References 32 and 33. [b] At 25°. [c] At 20°.

benzene concentration is increased at constant temperature. Table V gives the dielectric constants (see ref 32, 33) for all the pure compounds which were used in these experiments.

Although we did not make detailed studies upon the change in the bulk dielectric constants for all systems investigated, we believe on the basis of the above table that one should expect a decrease in the bulk dielectric constant of THF or DME solution as the neutral aromatic compound concentration is increased.[34] An increase in rate with a decrease in the bulk dielectric constant of the medium can be qualitatively explained theoretically using a number of simple transition state models which predict $\ln k \propto (1/D)$ for reactions between ions and neutral molecules. However, the theory is far from quantitative.[35]

We have attempted to rationalize the calculated rate constants and activation energies in the following manner. We made use of experimental results obtained by Hirota and coworkers[36] upon the electron-transfer reaction in the naphthalenide–naphthalene systems. They have found that different types of ion pairs, i.e., "loose ion pairs," "solvent-separated ion pairs," and "tight ion pairs" exchange electrons at different rates with the neutral aromatic hydrocarbons in ether-like solvents. From this study they concluded that rate constants for electron transfer for loose ion pairs at 25° were of the order of 10^9 l./(mol sec) and for tight ion pairs ranged between 5×10^6 and 1×10^7 l./(mol sec). Activation energies ranged between 2.9 and 3.6 kcal for loose pairs and 4 and 6 kcal for tight ion pairs.

Comparison of our data and Hirota's results suggests that we have measured rate constants for electron-transfer reactions involving ion pairs. The reaction most likely can be expressed as

$$B^-M^+ + B \rightleftharpoons B + B^-M^+$$

where B is the benzene molecule and M^+ is the alkali metal counterion.

Since we believe the systems contain ion pairs, the electron-transfer reaction is considered to be essentially an ion-transfer reaction in the sense that the

counterion probably transfers in a correlated manner with the electron.[37] However, no alkali splittings were ever observed in the various benzene systems.[23] The computer simulations were tried in all cases with and without metal splittings included in the input of the program. Using natural line widths of about 0.1 G and splittings for a spin $^3/_2$ alkali ion of about 0.2 G gave the same results as using natural line widths of 0.9–1.0 G for spectra taken at 18°. Therefore, we did not include splittings due to metal ions but merely increased the effective natural line width to take into account what we believe to be the result of unresolved metal splittings contributing to the width of the lines in the absence of electron exchange.[25]

The rate constant and activation energy for the K, THF system are larger and smaller, respectively, than in the K, DME system at the same temperature and neutral benzene concentration. (Table III) This may indicate that the solvent (THF) solvates the alkali ion more so than in DME. This interaction with solvent molecules in the K, THF system could lead to the formation of solvent-separated ion pairs, whereas in the K, DME system a tighter ion pair might be formed.

Szwarc and coworkers[32,38,39] found that Na^+ ions have a larger solvated radius in THF as compared with DME (4.3 and 3.4 Å, respectively). No results were reported for K^+ ions but one might speculate that similar results would be found. On this basis the K, DME system should form tighter ion pairs and we believe the smaller rate constant is symptomatic of this.

In a preliminary report on the benzene–benzenide system[10] we analyzed our rate data using the simple limiting case (eq 2). At the time we noted that although the plot of ΔH vs. $[B]^{-1}$ was linear it did not extrapolate to zero line width at infinite concentration, as required by the simple formula. The limiting condition under which the formula is valid, i.e., $|w_i - w_j| \cdot \tau \ll 1$, is not fulfilled for benzene at lower concentrations and is only marginally fulfilled at higher concentrations where the spectrum is strongly exchange narrowed. A recent paper by Johnson and Holz[40] analyzes the shortcomings of eq 2 and illustrates ways of extending its usefulness. The authors also derive formulas useful for estimating errors and testing the validity of the second moment formula for particular compounds.

We have compared the computer-simulated rate constants derived from our data with those calculated using eq 2 for benzene reduced with the alloy in the mixed solvent. At the highest concentration of neutral benzene (narrowest line, $[B] = 5.5\ M$) the rate constant calculated by the simple formula method at 18° is about 6% larger than that found by computer simulation with the complete line shape formula. At the lowest concentration studied (broadest line, $[B] = 1.27\ M$) the rate constant calculated by the simple formula is almost 40% larger than that found by computer simulation (the same trend holds true for toluene also, see below). The agreement illustrated in Table I between computer-simulated rate constants and second moment rate con-

(32) C. Carvajal, K. J. Tolle, J. Smid, and M. Szwarc, J. Amer Chem. Soc., 87, 5548 (1965).

(33) "Handbook of Chemistry and Physics," 41st ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1960.

(34) Measurements of dielectric constant as a function of concentration for the system naphthalene–DME or naphthalene–THF do yield values substantially lower than the dielectric constants of the pure solvents at aromatic molecule concentrations appropriate to exchange narrowed solutions: unpublished results, G. E. Werner and W.H. Bruning. Also see C. J. F. Böttcher, "Theory of Electric Polarization," Elsevier Publishing Co., Amsterdam, 1952, pp 265–272.

(35) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp 534–536; K. J. Laidler, "Chemical Kinetics," 2nd ed, McGraw-Hill Book Co., New York, N. Y., 1965, pp 225–228; J. G. Kirkwood, J. Chem. Phys., 2, 351 (1934).

(36) N. Hirota, R. Carraway, and W. Schook, J. Amer. Chem. Soc., 90, 3611 (1968).

(37) F. C. Adam and S. I. Weissman, ibid., 80, 1518 (1958).

(38) M. Szwarc, Accounts Chem. Res., 2, 87 (1969).

(39) M. Szwarc, "Carbanions, Living Polymers and Electron-Transfer Processes," Interscience Publishers, New York, N. Y., 1968.

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

stants is expected since these data were obtained from spectra exhibiting quite sharp lines. Under such circumstances the limiting condition $|w_i - w_j|\tau \ll 1$ is amply fulfilled.

Thus, in this case the simple formula leads to rate constants which are too large, the error increasing as one approaches the intermediate region just before the reappearance of hyperfine structure. Linearities of plots of experimental line width vs. reciprocal of concentration of the neutral material have been suggested as an adequate test of the simple equation if they extrapolate to a reasonable value of the natural line width in the absence of exchange.[40] However, because of the apparent concentration dependence of the rate constant noted in this work, linear behavior can still be obtained and a curve might extrapolate to a reasonable value for the line width in the absence of exchange and yet still yield incorrect values of the rate constant.

In the final analysis it seems that results obtained from the second moment formula or any extensions which depend upon simplification of the complete line shape expression through a limiting process, should be checked against computer-simulated spectra.

B. Toluene and p-Xylene Systems. The same type of rationalization can be applied to these systems as was applied to the benzene systems discussed above. They are similar in all respects to benzene except that variations in line width and coupling constant with temperature are small or nonexistent in the absence of electron exchange. Therefore, the uncertainty due to selection of these parameters is reduced as compared to benzene.

As the number of methyl groups increase on the benzene ring one experiences more difficulty in reducing the hydrocarbon and as indicated above, this limited the concentration and temperature range over which experiments could be carried out. However, a few conclusions could still be reached for these systems (see below, part C).

Both toluene and p-xylene are known to be ion paired in DME solution.[31,41] However, as in the case of benzene, the effect of the ion pairing was incorporated in the computer simulations by using a line width larger than what one would expect for a dilute hydrocarbon solution in the absence of chemical exchange effects.

The rate constants and activation energies obtained again support the notion that the electron-transfer reaction takes place between a neutral molecule and an ion-paired species. The activation energy for p-xylene is slightly larger in DME with K+ as counterion than for toluene under the same conditions.

C. Comparison of All Systems. We have noted the effects of solvent and reducing agent on the different compounds investigated in this work. One of our earliest objectives was to assess the effect of structural changes in molecular anion radicals on rate constants for electron transfer. Such information has proved exceedingly difficult to obtain for these types of electron-transfer reactions because of the difficulty of normalizing results for different anions and because of experimental errors. From this work we can compare rate

constants for benzene and p-xylene exchange under identical conditions of solvent, metal ion, neutral molecule concentration, and temperature. Values of rate constants at a neutral concentration of 4.77 mol/l. can be obtained from Figures 2 and 7 for benzene and p-xylene at 18°. (Unfortunately, the toluene system was not sufficiently stable at 18° to allow us to follow the apparent concentration dependence of k.)

At $18° k = 5.2 \pm 0.9 \times 10^7 M^{-1} sec^{-1}$ for (K, DME)-benzene and $k = 4.3 \pm 0.3 \times 10^7 M^{-1} sec^{-1}$ for (K, DME)-p-xylene. We believe that the smaller value for the p-xylene rate constant is statistically significant. Collisions leading to successful electron-transfer reactions in this system may be less likely to occur at every encounter between a neutral molecule and an anion than for the case of benzene, because of the blocking effect of the methyl groups or because of slight differences in ion-pair structure between the two solutions.

We hesitate to press this conclusion very far because it is not certain that the types of ion pairs formed in the benzene solutions are completely analogous to those formed in the p-xylene solutions. As mentioned earlier, ion-pair splittings cannot be observed for benzene.[42] At least one possible explanation has been advanced for this behavior.[25] It seems possible that even though introduction of methyl groups into aromatic anion-radical precursors still allows one to rationalize the behavior of hyperfine splitting constants and certain features of the optical spectra through simple theories utilizing small perturbations, this by no means should suggest that an alkylated anion and its nonalkylated parent form the same ion-pair structure in solution. Thus, until more is known about the dynamic structure of ion pairs and the factors which determine whether they are loose, solvent-shared, tight, etc., it will be very difficult to assess substitution effects upon electron-transfer rate constants.

The identity of the counterion interacting with the anions studied by us is still uncertain. Recent reports[43,44] indicate that some hydrocarbon anions ion-pair preferentially with K+ in dilute solutions, in the absence of electron transfer, and in solutions exhibiting exchange-collapsed spectra, even though Na+ ions are present. For naphthalene reduced with Na in DME, enough K+ is present as an impurity in the glass to form substantial amounts of a potassium–naphthalenide ion pair. In our benzene and toluene systems, even when reduced with Na/K alloy, this might suggest that the counterion is K+. If Na+ formed some type of closely associated ion pair, we might expect to observe Na+ splittings in the spectra under conditions of minimum electron transfer.

Summary and Conclusions

A technique has been described which allows one to calculate the rates of electron transfer for benzene, toluene, and p-xylene anion radicals by comparing computer-simulated spectra with experimentally ob-

(41) J. R. Bolton, private communication. Ion-pair interactions must be quite small for toluene since splittings are not resolved. Proof of ion pairing was obtained by accurate line shape analysis which indicated inhomogeneous broadening which could be simulated by including small metal splittings in a computer calculation of line shape.

(42) K. W. Böddeker, G. Lang, and U. Schindewolf, *Angew. Chem. Intern. Ed. Engl.*, **6**, 954 (1968); *Angew. Chem.*, **80**, 998 (1968). With added LiCl, these authors have reported resolution of Li+ splittings in K-reduced solutions of benzene in 1:1 THF–DME. However, the solutions rapidly decay to biphenyl anion. We attempted no electron transfer studies on Li–benzene systems because of their unstable nature.

(43) P. Graceffa and T. R. Tuttle, Jr., *J. Chem. Phys.*, **50**, 1908 (1969).

(44) G. E. Werner and W. H. Bruning, *ibid.*, **51**, 4170 (1969).

tained spectra. Small rate constants and relatively large activation energies were found. This suggests ion-pairing effects are important in the benzene, toluene, and p-xylene systems investigated.

At present large experimental errors involved in experiments of this type do not allow one to assess very accurately the effects of changes in system parameters upon rate constants. More sophisticated observation techniques involving spectrum averaging devices and accurate frequency and field measuring equipment, all coupled with computer simulation, should soon allow one to investigate the more subtle aspects of such electron-transfer reactions. The experimental difficulties are probably at a maximum for the systems we have studied, although the time involved in computer simulation is a minimum because of the relatively small number of hyperfine energy levels to deal with for these

molecules. More ambitious studies with larger, more easily prepared and more stable anions should lead to important chemical information and are in progress.

Chemical Ionization Mass Spectrometry. XII. Alcohols

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Abstract: The isobutane chemical ionization mass spectra of 23 saturated, monohydroxylic alcohols have been determined. The ionization chamber temperature was 180°. The main ions produced are $(M - 17)^+ = R^+$ of ROH, $(M - 1)^+$, $(M + 1)^+$, $(M + 39)^+$, $(M + 57)^+$, and $(2M + 1)^+$. The relative intensities of the several ions depend upon the structure of the alcohol. For alcohols with three or fewer carbon atoms the $(M + 1)^+$ ion dominates the spectrum, but for alcohols with five or more carbon atoms the R^+ ion dominates. Thus for the larger alcohols the chemical ionization technique emphasizes the hydrocarbon portion of the molecule. The $(M + 39)^+$ intensity is significantly larger in the secondary alkanols with five or more carbon atoms than in the corresponding primary alkanols. By contrast the $(M + 57)^+$ ion is larger in the primary alkanols. The magnitude of the total ionization of the alcohols depends on the structure and is significantly smaller for the primary alcohols. Speculations on the origin of the observed relations between structure and spectra are given.

As part of a program in these laboratories to determine the chemical ionization mass spectra of different types of compounds, we have measured the isobutane chemical ionization spectra of a number of alcohols, and we here report the results of the investigation. The study is of the nature of a survey in that the spectra of a relatively large number of alcohols have been determined to establish general behavior patterns in a qualitative or semiquantitative manner.

In some preliminary investigations which have been partially reported,[1] it was found that when methane is used as the reactant in the chemical ionization technique extensive decomposition of the alcohols occurs, and in particular the intensity of ions in the molecular weight region (the quasi-molecular ions) tends to be rather small. To diminish the amount of fragmentation occurring, the present investigation was made using isobutane as reactant. As we have pointed out previously,[2] the main ion in the isobutane plasma is

$t\text{-}C_4H_9^+$. In our experience so far this ion often acts as a Brønsted acid, and it is a much milder protonating agent than the CH_5^+ and $C_2H_5^+$ ions found in methane plasma.

More details about the chemical ionization technique may be found in recent articles.[3,4]

Experimental Section

The spectra were obtained with the Esso chemical physics mass spectrometer.[1,5] All measurements were made at a single ionization chamber temperature, namely, 180°. The isobutane was research grade material obtained from Lif-O-Gen Co. of Lumberton, N. J. Its pressure in the ionization chamber of the mass spectrometer was maintained at 0.50 ± 0.01 Torr, and it was demonstrated that the spectra of the alcohols did not change significantly over the pressure range 0.5–0.7 Torr.

The alcohols used were obtained from the laboratory library of pure compounds, and the samples used were for the most part API standard samples or were samples from the Standards Project on Oxygenated Compounds of the Pennsylvania State University. Smaller alcohols such as methanol, ethanol, etc., were obtained from conventional commercial sources. For all of the compounds

(1) M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **88**, 2621 (1966).
(2) F. H. Field, *ibid.*, **91**, 2827 (1969).

(3) F. H. Field, *Accounts Chem. Res.*, **1**, 42 (1968).
(4) F. H. Field, *Advan. Mass Spectrom.*, **4**, 645 (1968).
(5) F. H. Field, *J. Amer. Chem. Soc.*, **83**, 1523 (1961).