Acknowledgment. We thank the National Science Foundation (Grant No. CHE77-07665 and CHE77-07808) for support.

References and Notes

(1) (a) Princeton University; (b) Clemson University; (c) Department of Chemistry, Tulane University, New Orleans, La. 70118.

(2) P. Finocchiaro, D. Gust, W. D. Hounshell, J. P. Hummel, P. Maravigna, and K. Mislow, *J. Am. Chem. Soc.*, **98**, 4945 (1976).

(3) D. A. Dougherty, K. Mislow, J. F. Blount, J. B. Wooten, and J. Jacobus, *J. Am. Chem. Soc.*, **99**, 6149 (1977).

(4) D. A. Dougherty, F. M. Llort, K. Mislow, and J. F. Blount, *Tetrahedron*, **34**, 1301 (1978).

(5) S. Brownstein, J. Dunogues, D. Lindsay, and K. U. Ingold, *J. Am. Chem. Soc.*, **99**, 2073 (1977); L. Lunazzi, D. Macciantelli, F. Bernardi, and K. U. Ingold, *ibid.*, **99**, 4573 (1977).

(6) P. Finocchiaro, W. D. Hounshell, and K. Mislow, *J. Am. Chem. Soc.*, **98**, 4952 (1976).

(7) N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, **73**, 679 (1948).

(8) D. E. Woessner, *J. Chem. Phys.*, **37**, 647 (1962).

(9) D. Wallach, *J. Chem. Phys.*, **47**, 5258 (1967).

(10) K. H. Valiev and M. M. Zaripov, *Zh. Eksp. Teor. Fiz.*, **42**, 503 (1962).

(11) H. Shimizu, *J. Chem. Phys.*, **37**, 765 (1962).

(12) W. A. Steele, *J. Chem. Phys.*, **38**, 2411 (1963).

(13) H. Shimizu, *J. Chem. Phys.*, **40**, 754 (1964).

(14) H. Versmold, *Z. Naturforsch., A*, **25**, 367 (1970).

(15) M. D. Zeidler, *Ber. Bunsenges. Phys. Chem.*, **69**, 659 (1965).

(16) H. G. Hertz, *Ber. Bunsenges. Phys. Chem.*, **74**, 666 (1970).

(17) D. E. Woessner, B. S. Snowden, Jr., and G. H. Meyer, *J. Chem. Phys.*, **50**, 719 (1969).

(18) R. Freeman and H. D. W. Hill, *J. Chem. Phys.*, **51**, 3140 (1969).

(19) A. Abragam, "The Principles of Nuclear Magnetism", Clarendon Press, Oxford, 1961, p 314. The asymmetry parameter (η) is assumed to be small.

(20) Quadrupole coupling constants observed for deuterons in a number of sp^3 hybridized systems are ca. 160 kHz. For example: CDH_2OH, $Q_D = 158.9 \pm 2.9$ kHz;[21] CDH_2CN, $Q_D = 156.1 \pm 3.0$ kHz;[21] CDH_2I, $Q_D = 163.1 \pm 3.8$ kHz.[22] Those for deuterons in sp^2 hybridized systems are ca. 210 kHz, e.g., C_6D_6, $Q_D = 196.5 \pm 1.3$ kHz;[23] C_6H_5D, $Q_D = 207.0 \pm 1.9$ kHz.[24]

(21) J. B. Wooten, A. L. Beyerlein, J. Jacobus, and G. B. Savitsky, *J. Chem. Phys.*, **65**, 2476 (1976).

(22) J. B. Wooten, J. Jacobus, G. B. Savitsky, and A. L. Beyerlein, *J. Chem. Phys.*, **66**, 4226 (1977).

(23) P. Diehl and C. L. Khetrapal, *Can. J. Chem.*, **47**, 1411 (1969).

(24) J. B. Wooten, A. L. Beyerlein, J. Jacobus, and G. B. Savitsky, *J. Magn. Reson.*, in press.

(25) For an isotropically reorienting molecule a single rotational diffusion coefficient (D_{iso}) suffices to describe the molecular reorientation. The correlation time is defined as $\tau_{iso} = (6D_{iso})^{-1}$.

(26) Variable temperature studies[3] of $^3J_{HH}$ (the vicinal ethano coupling constant) indicate that this coupling is invariant with temperature over the range 310–370 K in toluene. This observation rules out an appreciable population of the gauche conformer over the experimental temperature range reported here; otherwise, the magnitude of $^3J_{HH}$ would be expected to decrease with increasing temperature.

(27) A theoretical basis for this assumption has been presented by Steele[28] in terms of rotational friction coefficients. Recently, an inverse proportionality of moments of inertia and diffusion coefficients has been employed.[29,30] There appears to be no theoretical justification for this assumption; the authors of ref 29 employed this particular proportionality for the special purpose of amplifying an expected anisotropy, and those of ref 30 provided no justification for its use.

(28) W. A. Steele, *J. Chem. Phys.*, **38**, 2404 (1963).

(29) R. L. Somorjai and R. Deslauriers, *J. Am. Chem. Soc.*, **98**, 6460 (1976).

(30) M. Baldo, A. Forchioni, K. J. Irgolic, and G. C. Pappalardo, *J. Am. Chem. Soc.*, **100**, 97 (1978).

(31) T. K. Chen, A. L. Beyerlein, and G. B. Savitsky, *J. Chem. Phys.*, **63**, 3176 (1975).

(32) S. W. Collins, T. D. Alger, D. M. Grant, K. F. Kuhlmann, and J. C. Smith, *J. Phys. Chem.*, **79**, 2031 (1975).

(33) S. Berger, F. R. Kreissl, D. M. Grant, and J. D. Roberts, *J. Am. Chem. Soc.*, **97**, 1805 (1975).

(34) J. B. Wooten, A. L. Beyerlein, J. Jacobus, and G. B. Savitsky, *J. Am. Chem. Soc.*, **98**, 6490 (1976).

(35) D. R. Bauer, G. R. Alms, J. I. Brauman, and R. Pecora, *J. Chem. Phys.*, **61**, 2255 (1974).

(36) The ground-state geometry[3] was employed in this calculation. The two pertinent angles required in the Woessner equation[17] are the angle subtended by the internal rotational axis (along the para C–D bond) and the unique molecular reorientation axis (the z axis) and the angle subtended by the reorienting ortho C–D bond and the internal rotational axis. The values of these angles are 83.4 and 60°, respectively. Since all parameters for the calculation of the ratio τ_o/τ_p, except D_i, are therefore known, it becomes possible to solve the general Woessner equation[17] for D_i to obtain the experimental value of this ratio.

(37) Not only is "windmilling" highly improbable for obvious steric reasons, but it is also precluded on grounds of symmetry. For a pertinent discussion of "free rotation", see ref. 38.

(38) J. Reisse, R. Ottinger, P. Bickart, and K. Mislow, *J. Am. Chem. Soc.*, **100**, 911 (1978).

(39) Baldo et al.[30] have recently employed this approximation in treating internal rotation in the diphenyl dichalconides (PhX–XPh; X = S, Se, Te). For these molecules, τ_o/τ_p equals 1.28, 1.84, and 2.04, respectively. It should be noted that two of the D_i/D_{iso} ratios given in Table IV of ref 30 are incorrect; the values given for $(PhSe)_2$ and $(PhTe)_2$ should be 2.84 and 3.65, respectively, rather than 1.74 and 2.18.

(40) R. N. Renaud, D. Kovachic, and L. C. Leitch, *Can. J. Chem.*, **39**, 21 (1961).

(41) E. D. Schmid and F. Langenbucher, *Spectrochim. Acta*, **22**, 1621 (1966).

(42) R. Ratcliffe, and R. Rodehorst, *J. Org. Chem.*, **35**, 4000 (1970).

(43) C. E. Castro, *J. Am. Chem. Soc.*, **83**, 3262 (1961).

Equilibria Involving Cation Radical Ion Pairs

Ignacio J. Ocasio and Paul D. Sullivan*

Contribution from the Department of Chemistry,
Ohio University, Athens, Ohio 45701. *Received May 15, 1978*

Abstract: The equilibrium constants for the dissociation of cation radical ion pairs of 1,2,4,5-tetramethoxybenzene, phenothiazine, and 1,4-dimethoxyanthracene with I_3^- have been measured at −20 °C [$K_d = (1.54 \pm 0.16) \times 10^{-2}$, $(9.7 \pm 2.0) \times 10^{-2}$, and $(4.08 \pm 1.17) \times 10^{-1}$, respectively]. The equilibrium constants were measured by following the changes in g value on addition of varying amounts of I_3^- to solutions of the free radical.

Ever since the first EPR investigations of ion pairs by Adam and Weissman[1] and Atherton and Weissman[2] a great deal of data concerning the structure and thermodynamic parameters controlling the dissociation of organic anion radical ion pairs has appeared in the literature. Four different EPR techniques have been used to determine the ion pair dissociation constants. These include the use of (1) coupling constants,[3-5] (2) line widths (relaxation times),[6] (3) line intensities (spin concentrations),[7-9] (4) g values.[10] Of these, the use of g values has proved to be the most accurate method. The method consists basically of the ability to observe a smooth change in the g value of a radical as a function of counterion concentration and requires the generation of the "free" radical when the concentration of the counterion is zero. The use of EPR g values for the determination of equilibrium constants has also been demonstrated for solvent exchange equilibria.[11]

To date, similar information for cation radical ion pairs has not been available owing to the limited experimental observation of such species.[12-15] Romans et al.[12] first reported a g shift as a function of solvent for the tetramethylhydrazine cation radical produced by iodine oxidation which they at-

0002-7863/79/1501-0295$01.00/0

tributed to a cation radical–halide ion interaction. Sorensen and Bruning[13] measured the rates of electron transfer between radical cations and their parent molecules for phenothiazine (PTH) and tri-*p*-tolylamine and observed a dependence of the rate on the dielectric constant of the solvent mixture. This was attributed to ion pairing between the organic cation and the inorganic anion. Fajer et al.[14] observed halide ion splittings in some metalloporphyrin cation radical EPR spectra in solvents of low dielectric constant. This observation is probably more consistent with a complex formation between the cation radical and the halide anion rather than ion-pair formation. More recently, Goez-Morales and Sullivan[15] observed large shifts in the *g* value caused by halide ion interaction with the 1,2,4,5-tetramethoxybenzene (TMB) cation radical.

Because of the growing recognition of the importance of cation radicals as intermediates in many oxidation processes,[16] it is of fundamental interest to evaluate, if possible, the thermodynamic parameters controlling the dissociation of cation radical ion pairs. It seemed most appropriate to begin these studies with the TMB cation radical–halide anion ion pair system owing to the large *g* shift observed as a function of halide ion concentration.[15] This suggested that the use of Stevenson's *g*-value method for determining equilibrium constants might be applicable to this system. In this paper we wish to report the results of our experiments which have allowed us to determine for the first time an equilibrium constant for the dissociation of a cation radical ion pair (β) into a solvated ("free") cation radical (α) and a solvated anion:

$$\beta \rightleftarrows \alpha + X^- \qquad (1)$$

Experimental Section

1,2,4,5-Tetramethoxybenzene (TMB) was obtained as described previously.[15] Phenothiazine (PTH), 2,3,6,7-tetramethoxythianthrene (TMTH), 9,10-dimethoxyanthracene (9,10-DMA), 1,4-dimethoxyanthracene (1,4-DMA), iodine, alkali metal iodides, and nitromethane were obtained commercially and used without further purification. The iodides were dried in a vacuum oven at 100 °C for 72 h prior to use. Nitromethane was dried over molecular sieves and carefully degassed by repeated freeze–pump–thaw cycles before use. Solutions of triiodides were prepared by dissolving equimolar amounts of I_2 and the metal iodides in nitromethane.[17]

The oxidations were carried out in the following manner. A 0.010 M TMB solution (0.30 mL) was placed in one arm of an inverted U-tube (the other arm being drawn into a capillary tube) to which was added a trace of $AlCl_3$. The characteristic color of the TMB cation radical was then observed. The total volume was made up to 0.60 mL with varying amounts of the triiodide solution and pure nitromethane. This yielded a series of solutions with a constant concentration of TMB, but varying I_3^- concentrations. The resulting solution was then evacuated and degassed and transferred to the capillary tube which was placed in the EPR cavity at −20 °C. This temperature was used to ensure the stability of the cation radical. The EPR spectra were recorded on a Varian E-15, X-band spectrometer. The *g* factors were measured in a dual sample cavity as described previously,[15] using the perylene anion radical (g = 2.002 671 ± 0.000 003)[18] as a secondary standard.

Results

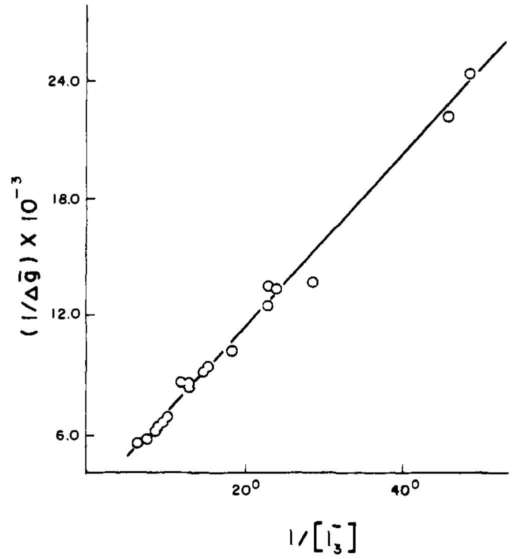

Figure 1. Plot of $1/\Delta\bar{g}$ vs. $1/[I_3^-]$ for $TMB^{+}\cdot I_3^-$.

Table I. *g* Shifts as a Function of the I_3^- Concentration for the $TMB/AlCl_3$ System[a]

I_3^-, M × 10^3	$\Delta\bar{g}$ × 10^5	I_3^-, M × 10^3	$\Delta\bar{g}$ × 10^5
2.07	4.1[b]	4.33	8.0
2.17	4.5	5.42	9.8
3.47	7.3	6.50	10.5
4.15	7.4	6.74	10.9

[a] Only some representative points are given. [b] $\Delta\bar{g} = g_{obsd} - g_{free}$, where g_{free} = 2.003 959.

Addition of NaI_3 solution while maintaining the TMB concentration constant results in a gradual increase of the observed *g* value as shown in Table I and Figure 1. This *g*-value shift can be interpreted in terms of an equilibrium between the cation radical ion pair (β) and the "free" cation radical (α) and a solvated anion (eq 1), if several assumptions are made. First, it is assumed that $AlCl_3$-oxidized TMB results in the production of a "free" cation radical (see Discussion section). Second, the time between ion association and dissociation is assumed fast on the EPR time scale. The observed *g* shift ($\Delta\bar{g}$) is then a weighted average of the *g* shift of the ion-paired species ($\Delta g'$) and that of the free ion (which would be zero). Using the two-jump model, the following expression has been derived:[10]

$$1/\Delta\bar{g} = (K_d/\Delta g'[I_3^-]) + 1/\Delta g' \qquad (2)$$

where $K_d = (\alpha)[I_3^-]/(\beta)$. A plot of $1/\Delta\bar{g}$ vs. $1/[I_3^-]$ should be linear and have a slope of $K_d/\Delta g'$ and an intercept of $1/\Delta g'$. As can be seen from Figure 1, our data do yield a straight line from which the dissociation constant was calculated to be (1.54 ± 0.16) × 10^{-2} at −20 °C. In order to eliminate the possibility that NaI_3 is ion paired in nitromethane the whole series of alkali triiodides and ammonium triiodide were examined in the same way yielding the results shown in Table II.

Similar experiments were also carried out with several other cation radicals. Phenothiazine cation radical ($PTH^{+}\cdot$), which has previously been suggested to form ion pairs with I_3^- in mixed solvent systems,[13] showed similar *g* shifts to those of TMB. A plot of $1/\Delta\bar{g}$ vs. $1/[I_3^-]$ was linear (see Figure 2) and a dissociation constant of (9.7 ± 2.0) × 10^{-2} at −20 °C was obtained. $1,4\text{-}DMA^{+}\cdot$ also showed *g* shifts on interaction with I_3^- and from the plotted data (Figure 3) a dissociation constant of (4.08 ± 1.17) × 10^{-2} at −20 °C was evaluated. $9,10\text{-}DMA^{+}\cdot$ and $TMTH^{+}\cdot$ were also investigated but did not show any shift in *g* values on addition of I_3^-.

Discussion

Free Ion–Ion Pair Equilibria. In the above analysis it was assumed that the equilibrium being measured was between the "free" ion and an ion-paired species. The "free" ion is assumed to be formed when TMB is oxidized by $AlCl_3$ in nitromethane. Although it must be noted that the nature of the counteranion is not known in $AlCl_3$-oxidized systems,[16] no effects directly attributable to the formation of ion pairs have ever been observed in such systems.[19] Additionally, the method of preparation of $TMB^{+}\cdot$ involved the use of only a trace of $AlCl_3$, thus

Table II. Dissociation Constant for $\mathrm{TMB^{+}\cdot/I_3^-}$ as a Function of Added Salt

salt	$K_d \times 10^2$
$\mathrm{LiI_3}$	>10
$\mathrm{NaI_3}$	1.56 ± 0.16[a]
$\mathrm{KI_3}$	2.76 ± 0.88
$\mathrm{RbI_3}$	0.95 ± 0.19
$\mathrm{CsI_3}$	2.22 ± 0.29
$\mathrm{NH_4I_3}$	1.93 ± 0.19

[a] Errors represent standard deviation of least-squares fit.

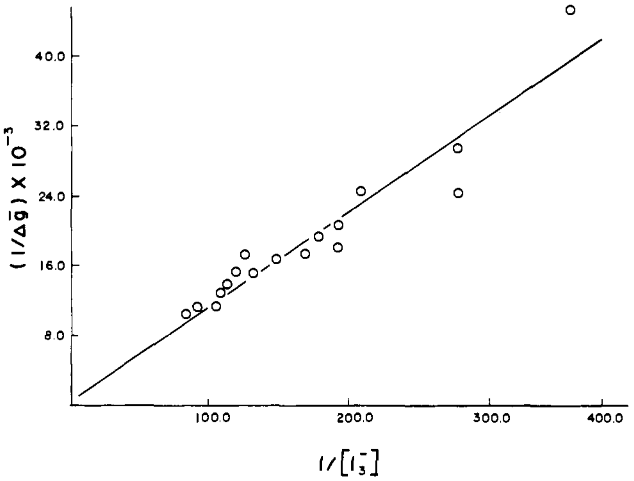

Figure 2. Plot of $1/\Delta g$ vs. $1/[\mathrm{I_3^-}]$ for $\mathrm{PTH^{+}\cdot I_3^-}$.

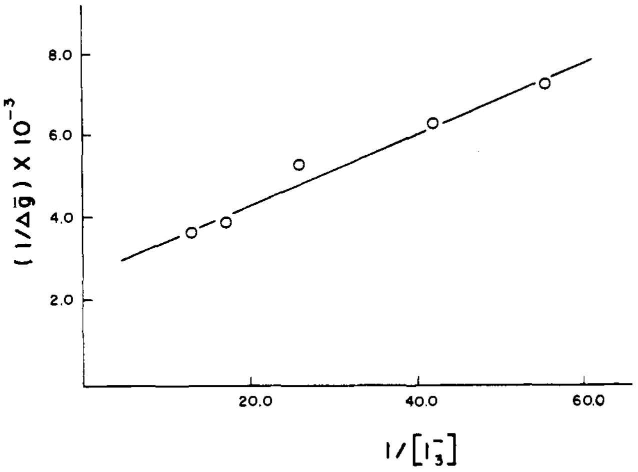

Figure 3. Plot of $1/\Delta g$ vs. $1/[\mathrm{I_3^-}]$ for $\mathrm{1,4\text{-}DMA^{+}\cdot I_3^-}$.

creating an extremely dilute solution. In a highly polar solvent such as nitromethane this should result in a shift of the ion-pair equilibrium, if it exists, toward "free" ions. This contention is further supported by some recent work on the dissociation of trityl cation ion pairs which indicated that essentially "free" ions exist in dilute solutions in nitromethane.[20]

It is true that many inorganic salts are ion paired in nitromethane[21-24] and this has been attributed to the low donor number of the solvent (2.7).[21] However, it has been suggested that in general the triiodide salts behave as strong electrolytes in nonaqueous solvents.[25] Further, the conductance of tetramethylammonium triiodide in nitromethane has been studied by Walden and Birr[27] and their results were in good agreement with the Onsager theory. However, Popov and Baum[24] recently suggested that a certain degree of ion pairing may exist for lithium triiodide in nitromethane.

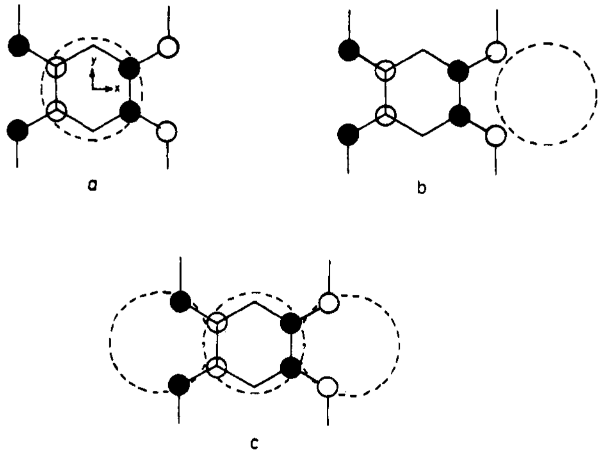

Figure 4. Possible structures of $\mathrm{TMB^{+}\cdot}$ ion pairs.

Table II shows the results for the dissociation constants of the $\mathrm{TMB^{+}\cdot/I_3^-}$ ion pair in nitromethane as a function of the countercation. All the values are very similar except for $\mathrm{LiI_3}$. The constancy of K_d with countercation is consistent with the hypothesis that the triiodides are essentially completely dissociated in nitromethane.[25,26] The $\mathrm{LiI_3}$ result is in accord with the suggestion of Popov[24] that this salt exhibits a degree of ion pairing in nitromethane.

The measured dissociation constants of the cation radical ion pairs are also of the same order of magnitude as those measured for anion radical ion pairs. For example, $K_d = (7.6 \pm 0.9) \times 10^{-1}$ for the potassium, 2,6-di-*tert*-butylsemiquinone anion ion pair in hexamethylphosphoramide.[10]

The possibility that other equilibria such as disproportionation of the radical cations might be coupled to the ion-pair dissociation was also considered.[28] There are not many documented examples of disproportionation constants for cation radicals; however, those that have been measured are generally very small[29-31] (e.g., thianthrene cation radical $K_{\mathrm{disp}} = 2.3 \times 10^{-9}$), thus suggesting that this equilibrium is probably not likely to affect the ion-pairing equilibrium.

For the above reasons we believe that the measured dissociation constants do indeed represent the dissociation of an ion pair into a free cation radical and a halide anion.[32]

Structure of the Ion Pair. Several observations of this work and our previous work[15] have implications with regard to the structure of the cation radical-halide anion ion pair. Previously it has been proposed[12,15] that the mechanism of oxidation of TMB by $\mathrm{I_2}$ involves the formation of a charge transfer complex between $\mathrm{I_2}$ and TMB (eq 3) which then reacts with another $\mathrm{I_2}$ molecule forming the TMB cation radical and $\mathrm{I_3^-}$ ion (eq 4). This species is subsequently solvated (eq 5).

$$\mathrm{TMB + I_2 \rightleftarrows TMB\cdot I_2} \tag{3}$$

$$\mathrm{TMB\cdot I_2 + I_2 \rightleftarrows TMB^{+}\cdot I_3^- + I\cdot} \tag{4}$$

$$\mathrm{TMB^{+}\cdot I_3^- + S(solvent) \rightleftarrows TMB^{+}\cdot(solv) + I_3^-(solv)} \tag{5}$$

Thus the observed g shifts were attributed[15] to the interaction of $\mathrm{I_3^-}$ and $\mathrm{TMB^{+}\cdot}$. The addition of NaI to TMB-$\mathrm{I_2}$ mixtures resulted in an increased g shift due to the increased concentration of $\mathrm{I_3^-}$ caused by reaction 6.

$$\mathrm{I^- + I_2 \rightleftarrows I_3^-} \tag{6}$$

By contrast, as part of our present study NaI was added to $\mathrm{AlCl_3}$-oxidized TMB solutions, and no shift in the g value of $\mathrm{TMB^{+}\cdot}$ was observed. This can be taken as further support for the idea that $\mathrm{I_3^-}$ is the counteranion in the $\mathrm{I_2}$-oxidized TMB solutions. However, it is perhaps somewhat surprising that $\mathrm{I^-}$, being a smaller anion with a more localized charge density, does not show any manifestation of ion-pair formation in terms of an observable *g* shift. This can be rationalized by considering the orbital symmetries of the cation and anion and the possible structures of the ion pair. The highest occupied molecular orbital (HOMO) of TMB, from which one electron is removed to form $TMB^{+}\cdot$, has a nodal plane passing through carbons 3 and 6 (Figure 4a). If the ion pair with I^- has a structure in which the counteranion is placed on the *yz* nodal plane (such as Figure 4a) or in which the anion vibrates symmetrically with respect to this plane, there will be no net overlap between the p orbitals on I^- and the π orbital of $TMB^{+}\cdot$ and hence no observable *g* shift. If the ion pair were to have a structure in which the anion is located away from the *yz* plane (for example, Figure 4b) an appreciable overlap between the HOMO of $TMB^{+}\cdot$ and appropriate p orbitals on I^- could produce an observable *g* shift. The lack of an experimentally observed *g* shift is therefore consistent with ion-pair formation between $TMB^{+}\cdot$ and I^- if the structure of the ion pair is similar to Figure 4a.

If the $TMB^{+}\cdot$ and I_3^- ion pair were to have a structure analogous to the $TMB^{+}\cdot$ I^- ion pair (i.e., Figure 4c),[33] the observed *g* shift could be explained. Overlap between the nonbonding p orbitals of the terminal iodine atoms of appropriate symmetry with the HOMO of $TMB^{+}\cdot$ could result in a net transfer of electron density from I_3^- to $TMB^{+}\cdot$. Thus the excited-state TMB $I_3\cdot$ would mix with the ground-state $TMB^{+}\cdot$ I_3^- resulting in a large *g* shift.

The similar interactions noted for 1,4-$DMA^{+}\cdot$ and $PTH^{+}\cdot$ with I_3^- and the lack of interaction observed for $TMTH^{+}\cdot$ and 9,10-$DMA^{+}\cdot$ may also be related to the structure of the ion pairs. Further work on the effect of ion-pair structure on the magnitude of the *g* shift and on the effect of solvent on the equilibrium constant are currently underway.

Acknowledgment. This investigation was supported by Grant CHE-76-04166 from the National Science Foundation.

References and Notes

(1) F. C. Adam and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 1518 (1958).
(2) N. W. Atherton and S. I. Weissman, *J. Am. Chem. Soc.*, **83**, 1330 (1961).
(3) N. Hirota, *J. Phys. Chem.*, **71**, 127 (1967).
(4) A. M. Herman, A. Rembaum, and W. R. Carper, *J. Phys. Chem.*, 71, 2661 (1967).
(5) G. R. Stevenson and A. E. Alegria, *J. Phys. Chem.*, **78**, 1771 (1974).
(6) G. R. Stevenson, R. Concepcion, and I. Ocasio, *J. Phys. Chem.*, **80**, 861 (1976).
(7) G. R. Stevenson and L. Echegoyen, *J. Phys. Chem.*, **77**, 2339 (1973).
(8) G. R. Stevenson and I. Ocasio, *J. Am. Chem. Soc.*, **98**, 980 (1976).
(9) R. D. Allendoerfer and R. J. Papez, *J. Phys. Chem.*, **76**, 1012 (1972).
(10) G. R. Stevenson and A. E. Alegria, *J. Phys. Chem.*, **79**, 1042 (1975).
(11) T. Yonezawa, T. Kawamura, M. Ushio, and Y. Nakao, *Bull. Chem. Soc. Jpn.*, **43**, 1022 (1970).
(12) D. Romans, W. H. Bruning, and C. J. Michejda, *J. Am. Chem. Soc.*, **91**, 3859 (1969).
(13) S. P. Sorensen and W. H. Bruning, *J. Am. Chem. Soc.*, **95**, 2445 (1973).
(14) J. Fajer, D. C. Borg, A. Forman, R. H. Felton, L. Vegh, and D. Dolphin, *Ann. N.Y. Acad. Sci.*, **206**, 349 (1973).
(15) G. Goez-Morales and P. D. Sullivan, *J. Am. Chem. Soc.*, **96**, 7232 (1974).
(16) A. J. Bard, A. Ledwith, and H. J. Shine, *Adv. Phys. Org. Chem.*, **13**, 155 (1976).
(17) It has been shown that the equilibrium constant for $I_2 + I^- \rightleftarrows I_3^-$ is approximately 10^7 in nitromethane and acetonitrile. [See J. C. Manchon, *C. R. Acad. Sci., Ser. C*, 1123 (1968).]
(18) B. G. Segal and G. K. Fraenkel, *J. Chem. Phys.*, **43**, 4191 (1965).
(19) The observed small shifts in *g* value measured for $AlCl_3$-oxidized TMB in a variety of solvents[15] are believed to arise from solvent effects[11] rather than from effects of ion pairing.
(20) W. Geogolczyk, S. Slomkowski, and S. Penczek, *J. Chem. Soc., Perkin Trans. 2*, 1729 (1977).
(21) U. Mayer, *Coord. Chem. Rev.*, **21**, 159 (1976).
(22) R. M. Keekra and J. L. Andrews, *J. Am. Chem. Soc.*, **84**, 3635 (1962).
(23) C. P. Wright, D. M. Murray-Rut, and H. Hartley, *J. Chem. Soc.*, 199 (1931).
(24) R. S. Baum and A. I. Popov, *J. Solution Chem.*, **4**, 441 (1975).
(25) A. I. Popov and N. E. Skelly, *J. Am. Chem. Soc.*, **76**, 5309 (1954).
(26) This result is also consistent with a similar extent of dissociation of alkali metal triiodides in CH_3NO_2, although the literature suggests that they are completely dissociated.[25]
(27) P. Walden and E. J. Birr, *Z. Phys. Chem. (Leipzig)*, **163**, 263 (1932).
(28) The possible deprotonation of $PTH^{+}\cdot$ was also considered but it is known that this equilibrium is only important in very basic conditions and that the radical cation is very stable in acetonitrile. [See P. Hansen and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, 264 (1973).]
(29) S. Hunig, *Pure Appl. Chem.*, **15**, 109 (1967).
(30) O. Hammerich and V. D. Parker, *Electrochim. Acta*, **18**, 537 (1973).
(31) U. Svanholm, O. Hammerich, and V. D. Parker, *J. Am. Chem. Soc.*, **97**, 101 (1975).
(32) It should be noted that in all cases the measured K_d values have not been corrected for ionic strength effects. Since the solutions used were quite dilute ($<10^{-2}$ M) such corrections should be small.
(33) This structure assumes that both $TMB^{+}\cdot$ and I_3^- are planar species. This is substantiated for $TMB^{+}\cdot$ by the magnitude and temperature independence of the methoxyl group proton splitting constants which if they were nonplanar would have greatly reduced splittings and be quite temperature dependent (see P. D. Sullivan, *J. Phys. Chem.*, **74**, 2563 (1970)). The structure of I_3^- is known to be planar (see J. H. Perlstein, *Angew. Chem., Int. Ed. Engl.*, **16**, 519 (1977)).

Tunnelling in Collinear Light–Heavy–Heavy Reactions

Werner Jakubetz

Contribution from the Institut fur Theoretische Chemie und Strahlenchemie der Universitat, A-1090 Wien, Austria. *Received June 14, 1978*

Abstract: For reactions of Mu, H, D, or T with F_2 or Cl_2, mathematically one-dimensional unsymmetric Eckart barrier permeabilities calculated within the vibrationally adiabatic model agree extremely well with exact quantum collinear reaction probabilities using extended LEPS surfaces. The corresponding rate constants and activation energies, in the temperature interval 230–900 K, are also in very good agreement. Other approximations, e.g., the parabolic barrier, have also been tested but are found to be less suitable. In particular, assumption of conservation of vibrational energy leads to considerable errors.

I. Introduction

A large number of investigations of tunnelling effects in chemical reactions (see, e.g., ref 1–4) have employed correction factors relating to mathematically one-dimensional (M1D) potential barriers of the Eckart or Bell type, for which the permeabilities can be given in analytic form.[5-8] Depending on the choice of the underlying basic approach—mostly transition-state theory (TST)[1,2,9,10]—and reaction system—mostly $H + H_2$—there arise some problems that must be considered carefully in assessment of the utility of the tunnelling corrections. Among the points of interest in this respect are the choice of a correct potential surface when comparing with experi-

0002-7863/79/1501-0298$01.00/0