Ion Pairing Effects on Bis(Hydrazine) Intervalence Radical Cations

Stephen F. Nelsen* and Rustem F. Ismagilov

Contribution from the Department of Chemistry, University of Wisconsin, 1101 University Avenue, Madison, Wisconsin 53706-1396

Received: April 20, 1999; In Final Form: April 28, 1999

Three bis(2-*tert*-butyl-2,3-diazabicyclo[2.2.2]oct-3-yl) radical cation salts, bridged by 2,3,5,6-tetramethylbenzene-1,4-diyl (**1**$^+$PF$_6^-$), biphenylene-4,4′-diyl (**2**$^+$PF$_6^-$), and 9,9-dimethyl-fluorene-2,7-diyl (**3**$^+$NO$_3^-$) groups, have been studied in methylene chloride. The transition energy at band maximum (E_{op}) increases as concentration increases and when ^{n}Bu$_4{}^+$BF$_6^-$ is added, indicating that ion pairing increases E_{op}. The E_{op} data fit a simple ion pairing equilibrium, giving ion pairing equilibrium constants at 293 K of 3100, 3100, and 6100 M^{-1}, respectively. Electron-transfer rate constants measured by ESR are reported for 0.19 mM **2**$^+$PF$_6^-$ and for 1 mM **2**$^+$PF$_6^-$ and **3**$^+$NO$_3^-$ in the presence of 20 mM ^{n}Bu$_4{}^+$BF$_6^-$ in methylene chloride. Prediction of k_{ET} from the optical spectrum of **2**$^+$PF$_6^-$ containing excess ^{n}Bu$_4{}^+$BF$_6^-$ was made both assuming the optical ET is endoenthalpic by an amount calculated from the increase in E_{op}, and that $\Delta G° = 0$ (that is, that the ion pairing effect may be lumped into the electron transfer coordinate along with the vertical and solvent reorganization effects). The predicted rate constant for the latter is only a factor of 2.5 times larger the former, so both agree rather well with the ESR-derived rate constant.

Introduction

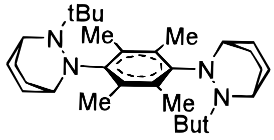
Ion pairing[1] affects many important chemical processes. For example, recent studies show that it can induce optical activity in synthetic polymers[2] and control enantioselective aldol condensations.[3] Most quantitative measures of ion pairing equilibrium constants (K_{IP}) have come from conductivity measurements, that require exceptional purity of both the salts studied and the solvent.[4] Such studies become increasingly difficult as the dielectric constant of the solvent decreases, and relatively little conductivity work has been done in nonpolar solvents, although the groups of Ashby and of Darenbourg have obtained impressively internally consistent conductivity data in tetrahydrofuran on alkali metal aluminum hydrides and transition metal carbonyl complexes that cannot be studied in polar solvents because they are too reactive.[5] More recent work on ion pairing has used nuclear Overhauser effects on NMR spectra, that provide structural information on the relative positioning of the ions, but do not give K_{IP} values.[6]

This work concerns ion pairing effects on electron transfer (ET) reactions. Ionic strength changes for polycationic ET systems are well-known to effect the rate constant for ET (k_{ET}) by changing the electrostatic work term.[7] Medium effects on ET reactions of metal-centered systems have been recently reviewed.[8] Pietrowiak and Miller found very large effects of changing the size of the cation when salts are added to systems in which radical anions of bifunctional compounds are generated by pulse radiolysis, and concluded that these effects are caused both by kinetic effects on anion generation and thermodynamic effects on intramolecular ET within radical anions generated.[9] Wahl's group pioneered the study of ion pairing effects on intermolecular self-exchange reactions of metal-centered compounds,[10a] and Wherland has reviewed ion pairing effects on metal-centered ET systems in nonaqueous solvents.[10b]

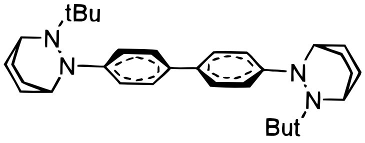
The simplest ET systems are symmetrical intervalence (IV) compounds that have the same charge-bearing units connected by a bridge, and are at an oxidation state causing these units to have charges that differ by one unit. The ET for these symmetrical, localized (Robin-Day Class III) IV compounds is intramolecular, with zero driving force. When the electronic coupling between the charge-bearing units (measured by the matrix coupling element *V*) is large enough, a charge-transfer (CT) band is observed, giving information about the adiabatic surface on which thermal ET occurs. Using Marcus−Hush theory, the transition energy at maximum intensity (E_{op}) corresponds to the total vertical reorganization energy for thermal intramolecular ET (Marcus' λ), and *V* can be estimated from the CT band parameters using Hush theory.[7] Transition metal-centered IV compounds have received by far the greatest study.[11] Ion pairing has been shown to increase E_{op} for dithiaspiro-bridged [Ru(NH$_3$)$_5$]$_2{}^{5+}$,[12] biferrocenium cation [(Fc)$_2{}^+$],[13] and FcC/CFc$^+$ systems,[14] and attributed to a positive free energy for ET within the ion-paired system, so E_{op} for an ion paired system is not λ, but $\lambda + \Delta G°$. In keeping with this idea, addition of small cation salts to [(NC)$_5$Fe^{III}-bis(pyridyl)-ethylene-Fe^{II}(CN)$_5$]$^{5-}$ in water resulted in an initial increase in E_{op}, followed by a decrease, back nearly to the initial value when very large amounts of LaCl$_3$ were added.[15] This behavior was interpreted as a result of equivalent ion pairing of both polyanions resulting in a zero free energy photo-ET again. No group has concluded that a simple ion pairing process was in fact present for the IV compound they studied. Conductivity measurements indicated an increase in ion pairing in the concentration range studied optically for Fc$_2{}^+$I$_3^-$ in nitrobenzene, but that it was mostly ion paired in methylene chloride, and the presence of higher ionic aggregates than simple ion pairs was suggested in methylene chloride.[13] Higher aggregates were also suggested from a dependence of E_{op} values extrapolated to infinite dilution on the oxidant used to generate the IV oxidation state for the ruthenium pentaammine system,[12c] and for FcC/CFc$^+$X$^-$ based on deviations of E_{op} versus [X$^-$] data from expectation for simple ion pairing equilibria.[14]

10.1021/jp991294h CCC: $18.00

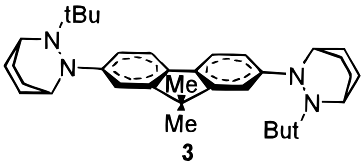
The present work concerns ion pairing effects on the IV bis(hydrazine) radical cations $\mathbf{1}^{+}-\mathbf{3}^{+}$ in methylene chloride. The



1



2



3

preparation, characterization, optical spectra and k_{ET} values measured in acetonitrile for these compounds have been discussed previously.[16] The principal feature that studying these compounds provides in addition to information from the previously studied transition metal-centered systems is that k_{ET} values can be measured because of the large λ values caused by the large internal reorganization energy of hydrazine units, so that how ion pairing affects the thermal as well as the optical rate constant for ET can be determined.

Results and Discussion

Ion Pairing Equilibria. Describing ion pairing for IV compounds quantitatively requires use of a large range of concentrations (by using more than one path length cell) and controlling the temperature. The E_{op} of $\mathbf{1}^{+}-\mathbf{3}^{+}$ in methylene chloride is observed to drift to higher values at higher concentrations, but not in acetonitrile. Equation 1 describes the

$$E_{\mathrm{op}} = (E_{\mathrm{op}}^{\ \mathrm{free}} + K_{\mathrm{IP}}[\mathbf{X}^{-}]E_{\mathrm{op}}^{\ \mathrm{IP}})/(1 + K_{\mathrm{IP}}[\mathbf{X}^{-}]) \qquad (1)$$

position of the band maximum if a simple ion pairing equilibrium $[\mathbf{A}^{+}] + [\mathbf{X}^{-}] \rightleftharpoons [\mathbf{AX}]$, characterized by an equilibrium constant K_{IP} is present, and if $\Delta E_{\mathrm{op}} = E_{\mathrm{op}}^{\ \mathrm{IP}} - E_{\mathrm{op}}^{\ \mathrm{free}}$ is small compared to the bandwidth (it is). Equation 1 assumes that the band maximum observed occurs at the weighted average for the free ion and ion pair positions, and was used by Shepherd and workers in studies of $\Delta G° \neq 0$ ligand-to-metal CT bands,[17] as well as in previous work on metal-to-metal CT bands.[14] In eq 1 $[\mathbf{X}^{-}]$ is the equilibrium concentration of independently solvated counterion, $[\mathbf{A}^{+}]$ is that of the intervalence compound, and $[\mathbf{AX}]$ the concentration of ion pair, while $E_{\mathrm{op}}^{\ \mathrm{free}}$ is the transition energy of independently solvated $[\mathbf{A}^{+}]$, and $E_{\mathrm{op}}^{\ \mathrm{IP}}$ that of the ion pair. Equation 2 gives the equilibrium concentration

$$[\mathbf{AX}] = [\mathbf{A}^{\mathrm{tot}}] - [\mathbf{A}^{+}] \qquad (2)$$

of **AX** in terms of the total stoichiometric concentration of both forms of **A** in the solution. It is important to distinguish $[\mathbf{A}^{\mathrm{tot}}]$ and $[\mathbf{X}^{\mathrm{tot}}]$ from $[\mathbf{A}^{+}]$ and $[\mathbf{X}^{-}]$. From eqs 1 and 2, eq 3 may be obtained for E_{op}, and was used in fitting the experimental data. Fit to eq 3 would not have to be observed for a real system, of course. Even if there were not ion pairing, increasing the

$$E_{\mathrm{op}} = \{2E_{\mathrm{op}}^{\ \mathrm{free}} + [(1 + 4K_{\mathrm{IP}}[\mathbf{A}^{\mathrm{tot}}])^{1/2} - 1]E_{\mathrm{op}}^{\ \mathrm{ip}}\}/\{1 + (1 + 4K_{\mathrm{IP}}[\mathbf{A}^{\mathrm{tot}}])^{1/2}\} \qquad (3)$$

concentration of charged species could make the solvent component of the reorganization (λ_{s}) larger, thus increasing λ and hence E_{op}. Such an effect might be detected before, or together with formation of triple ions or higher aggregates, and either would lead to deviations from fit to eq 3. Nevertheless, dilution experiments for $\mathbf{1}^{+}\mathrm{PF}_6^{-}$, $\mathbf{2}^{+}\mathrm{PF}_6^{-}$, and $\mathbf{3}^{+}\mathrm{NO}_3^{-}$ in methylene chloride at 293 K gave good fit to the simple ion pairing equilibrium of eq 3 (Figure 1), producing the fitting constants shown in Table 1.[18] It will be noted that the K_{IP} obtained from fitting to eq 3 is not very precise.[11,17]

Another type of experiment that we (as well as Blackbourn and Hupp)[14a] have done is to add an inert salt, that we will call **BX** (we added ${}^{n}\mathrm{Bu}_4\mathrm{N}^{+}\mathrm{PF}_6^{-}$ to $\mathbf{2}^{+}\mathrm{PF}_6^{-}$). The added salt will participate in an independent ion pairing equilibrium, $[\mathbf{B}^{+}] + [\mathbf{X}^{-}] \rightleftharpoons [\mathbf{BX}]$, characterized by an equilibrium constant $K_{\mathrm{IP,B}}$.

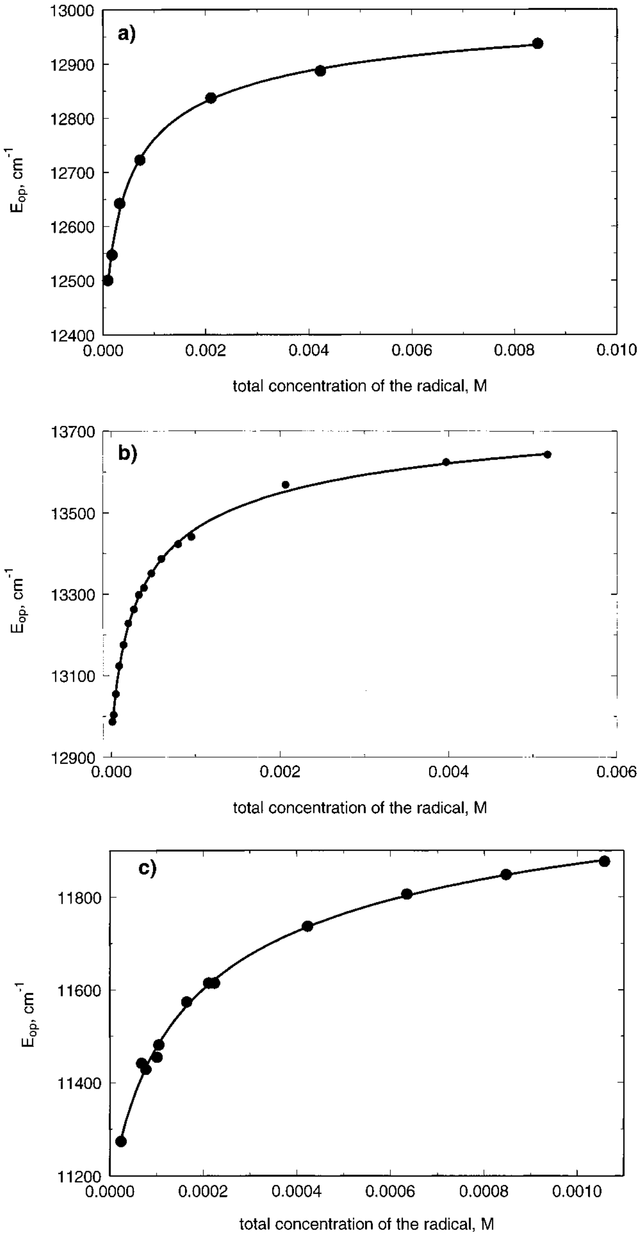


Figure 1. (a) E_{op} for solutions of $\mathbf{1}^{+}\mathrm{PF}_6^{-}$ in methylene chloride (points), and fit to eq 3 using the parameters shown in Table 1. (b) Same information for $\mathbf{2}^{+}\mathrm{PF}_6^{-}$. (c) Same information for $\mathbf{3}^{+}\mathrm{NO}_3^{-}$.

TABLE 1: Ion Pairing Data at 293 K in Methylene Chloride

species	**1**$^+$PF$_6^-$	**2**$^+$PF$_6^-$	**3**$^+$NO$_3^-$	^{n}Bu$_4$PF$_6^-$ [a]
K_{IP} (M^{-1})	3100 ± 1000^b	3100	6100	6300
$\Delta G°_{IP}$ (kcal/mol)	-4.7 ± 0.2	-4.7	-5.1	-5.1
E_{op}^{free} (cm^{-1})	$12\,365 \pm 35$	12 950	11 155	
E_{op}^{ip} (cm^{-1})	$13\,055 \pm 15$	13 845	12 224	
$\Delta G°_{ET,IP}$ (kcal/mol)	$+2.0 \pm \sim 0.1_4$	$+2.6$	$+3.0_5$	

[a] From E_{op} data for **2**$^+$PF$_6^-$ in the presence of added ^{n}Bu$_4$PF$_6^-$. [b] The errors quoted are larger than statistical error of the fit to eq 3, but more realistically represent what we believe the error to be.

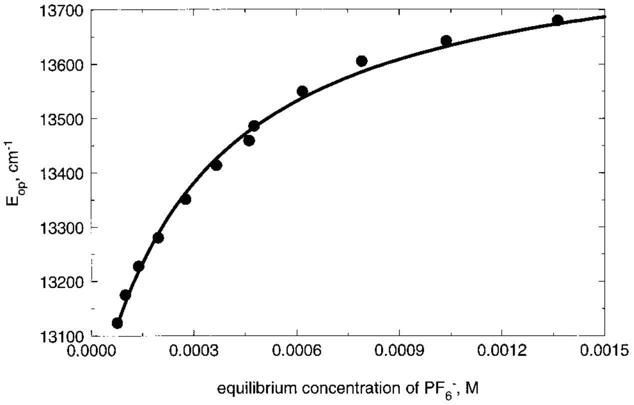


Figure 2. E_{op} for solutions of **2**$^+$PF$_6^-$ in methylene chloride versus free [PF$_6^-$], obtained by adding ^{n}Bu$_4$NPF$_6$ and fitting the data to eq 4.

The expression for [**X**$^-$] in the presence of both **AX** and **BX** is given by eq 4. Although the expression for E_{op} when both **AX** and **BX** are present can be solved analytically, the solution is too complex to be useful, and we used numerical solution to fit the experimental E_{op} data in this case. As expected, adding ^{n}Bu$_4$N$^+$PF$_6^-$ changes the E_{op} observed because two species of comparable K_{IP} are present. We note for IV salt having E_{op}^{free} and E_{op}^{IP} known in a given solvent, E_{op} will act as a sensor for free [**X**$^-$], and thus can be used to measure relative values of K_{IP} for the IV salt and an added inert salt. We know of no other technique by which data on the relative sizes of ion pairing constants in a solution containing two cations could be obtained. The experimental data for adding ^{n}Bu$_4$N$^+$PF$_6^-$ to **2**$^+$PF$_6^-$ in methylene chloride at 293 K gave a good fit to eq 4 (Figure 2), producing K_{IP}(^{n}Bu$_4$$-PF_6^-$) of ~6300 M^{-1}.

$$[\mathbf{X}^-] = \mathbf{A}^{tot}/(1 + K_{IP}[\mathbf{X}^-]) + \mathbf{B}^{tot}/(1 + K_{IP,B}[\mathbf{X}^-]) \quad (4)$$

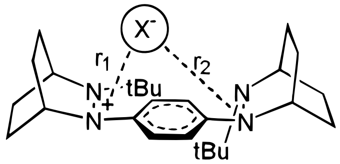
We know of no particularly good comparisons for the K_{IP} data of Table 1, as we have not found literature K_{IP} values in methylene chloride.[19] The only data we have seen for ^{n}Bu$_4$N$^+$ ion pairing in any nonpolar solvent is the K_{IP} for the BPh$_4^-$ salt in tetrahydrofuran (a solvent of slightly smaller dielectric constant [$\epsilon = 7.58$ D] than that of methylene chloride [$\epsilon = 8.93$ D]), where $K_{IP} = 23\,000$ M^{-1} ($\Delta G°_{IP} = -5.95$ kcal/mol) has been reported.[20] We observe very similar free energies for ion pairing (-4.7 to -5.1 kcal/mol) for all four salts studied here, suggesting that large differences in ion pairing free energies for such multiatom cations and anions are not present, and that considering electrostatic interactions is indeed appropriate. From conductivity measurements on ^{n}Bu$_4$N$^+$I$^-$,[4] K_{IP} drops from 2400 in pyridine ($\epsilon = 12.91$) to 3 in acetonitrile. Such small values are consistent with our inability to see any ion pairing effects on E_{op} in acetonitrile up to several millimolar concentrations for our IV compounds.

The fits to eq 3 also produce E_{op}^{free} and E_{op}^{IP}, allowing calculation of the increase in free energy for photo-ET between the hydrazine units in the free ion and the ion pair, $\Delta G°_{ET,IP}$ of Table 1. As expected, $\Delta G°_{ET,IP}$ is significantly less than $-\Delta G°_{IP}$. The size of $\Delta G°_{ET,IP}$ ought to be controlled by the difference in distance between the ion paired cationic hydrazine unit and the neutral hydrazine unit (between which an electron is transferred upon photo-ET). The alkyl groups of the hydrazine unit probably force the anion to lie over the aromatic ring, nearer to the oxidized nitrogen, on the opposite face as the *tert*-butyl group, so the distances from the anion to the hydrazine units are not extremely different (see **A**). $\Delta G°_{ET,IP}$ is observed to be smaller for the singly phenylene-bridged system **1**$^+$ than it is for the compounds with longer bridges, as expected because r_2 should differ more from r_1 for a longer bridge.

TABLE 2: ESR Rate Constant Data in Methylene Chloride

2$^+$PF$_6^-$ (0.19 mM)		**2**$^+$PF$_6^-$ (with 20 mM Bu$_4$N$^+$PF$_6^-$)		**3**$^+$PF$_6^-$ (with 20 mM Bu$_4$N$^+$PF$_6^-$)	
T^a	k_{ESR}^b	T^a	k_{ESR}^b	T^a	k_{ESR}^b
263	1.50	278	1.41	218.1	1.19
268	1.72	283	1.59	223.1	1.41
273	2.04	288	1.79	228.1	1.63
278	2.29	293	1.99	233.1	1.89
		298	2.20	238.1	2.16
		303	2.46		
$\Delta H^‡ = 3.6_5 \pm 0.43^c$		$\Delta H^‡ = 3.1_3 \pm 0.15^c$		$\Delta H^‡ = 2.6_1 \pm 0.09^c$	
$\Delta S^‡ = -7.0 \pm 1.6^d$		$\Delta S^‡ = -9.8 \pm 0.5^d$		$\Delta S^‡ = -9.0 \pm 0.4^d$	

[a] Unit: K. [b] Unit: 10^8 s^{-1}. [c] Unit: kcal mol^{-1}, error quoted at the 95% confidence level (statistical only). [d] Unit: cal mol^{-1} K^{-1}, error quoted at the 95% confidence level (statistical only).



A

Thermal and Optical Rate Constants. With K_{IP} values as large as those for these compounds, we cannot obtain ESR rate data in methylene chloride at low enough concentration that ion pairs are not present. For **2**$^+$PF$_6^-$, we obtained rate data at 0.19 mM (calculated 29% ion paired), and for both **2**$^+$PF$_6^-$ and **3**$^+$PF$_6^-$, at about 1 mM in the presence of 20 mM Bu$_4$N$^+$PF$_6^-$, where ion pairing is calculated to be essentially complete. These ESR rate constant data appear in Table 2. Increasing the amount of ion pairing clearly causes a decrease in k_{ESR} for **2**$^+$PF$_6^-$. The data are compared in the form of an Eyring plot in Figure 3. The 0.19 M "partially ion paired" solution gave k_{ESR} only a factor of 1.6 larger than that for the fully ion paired solution. The effect of ion pairing of **2**$^+$ on k_{ESR} is clearly rather small. We shall next consider whether an effect this small is predicted from the optical spectra.

More accurate estimation of k_{ET} from the optical spectra of our compounds (k_{OPT}) can be made by choosing diabatic potential energy surface shape that fits the CT band observed than by using the Marcus$-$Hush assumption that the diabatic potential energy surfaces are exactly parabolas.[16,22] We employed eq 5 for fitting the CT band data of these compounds.

$$H'_{aa} = \{\lambda/(1 + C)\}\{\mathbf{X}^2 + C(\mathbf{X})^4\} \quad (5a)$$

$$H'_{bb} = \{\lambda/(1 + C)\}\{(\mathbf{X} - 1)^2 1 + C(\mathbf{X} - 1)^4\} \quad (5b)$$

The exact function used for the diabatic energy surfaces to fit the CT band is not important for calculating k_{OPT} from an IV$-$

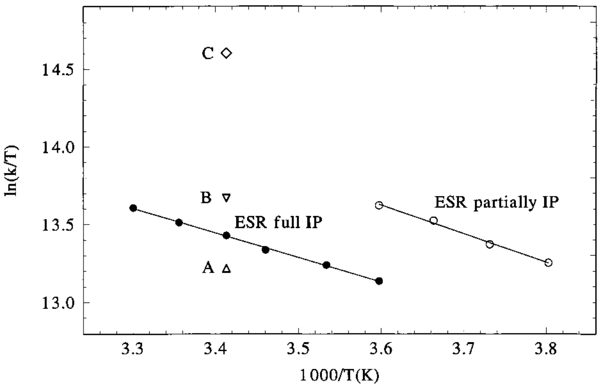


Figure 3. Eyring plot comparison of ESR-derived rate constants in methylene chloride (from Table 2) having as little ion pairing as we could manage (0.19 mM $\mathbf{2}^+PF_6^-$), and as much (1.0 mM $\mathbf{2}^+PF_6^-$ + 20 mM $^nBuN^+PF_6^-$), with k_{OPT} values calculated by the three methods of Table 4, using V_H for the matrix coupling element.

CT band, but properly fitting the CT band is important.[16,22] Using eq 5 is convenient and allows fitting the CT band as well as using the much more complex vibronic coupling theory (which introduces another parameter, because λ must be separated into λ_s and λ_v to apply it). It will be noted that eq 5 produces the Marcus−Hush parabolas at $C = 0$, so C is a measure of the observed bandwidth at half-height relative to the value for Marcus−Hush parabolas, $\Delta\nu_{1/2}^{HTL} = [16RT \ln(2)E_{op}]^{1/2}$. Our compounds have the same charge-bearing units, and therefore should have quite similar barrier crossing frequencies ($h\nu_v$). The barrier-crossing frequency $h\nu_v$ is considerably in excess of $2k_BT$ for these compounds (we used $h\nu_v = 800$ cm^{-1} successfully in calculating k_{OPT} for bis(hydrazine) cations).[16,21,22] Nevertheless, the IV−CT bandwidths in acetonitrile, where no ion pairing effects could be observed, differ considerably: $\mathbf{1}^+$, $C = 0.20$ at 293 K; $\mathbf{2}^+$ $C = 0.02$; $\mathbf{3}^+$ $C = -0.02_5$. It may be noted that the IV−CT band for $\mathbf{3}^+$ is slightly narrower than $\Delta\nu_{1/2}^{HTL}$, although $\mathbf{3}^+$ is clearly a localized IV compound.[16b] Our results make it clear that the deviation in bandwidth from $\Delta\nu_{1/2}^{HTL}$ is not principally controlled by $h\nu_v$, as has usually been assumed.[7]

TABLE 3: Optical Data for Ion Pairing at 293 K in Methylene Chloride

compd	$\mathbf{1}^+PF_6^-$	$\mathbf{2}^+PF_6^-$	$\mathbf{3}^+NO_3^-$
λ (kcal/mol)	35.8	37.2	32.25
C	0.24	0.11	0.13
V_H, kcal/mol[a]	3.23	3.44	4.26
ΔG^* (free ion)[b]	4.71	5.49	4.71
k_{OPT} (free ion)[c]	6.11×10^9	1.59×10^9	3.44×10^{10}
prediction for full ion pairing assuming $\Delta G° > 0$, but no change in ET parameters (method A):			
$\Delta G^*(IP)$[d]	5.74	6.82	5.23
$k_{OPT}(IP)$[e]	1.06×10^9	1.61×10^8	2.36×10^9

[a] Calculated using $d = 5.657$ Å for $\mathbf{1}^+$, 8.0 Å for $\mathbf{2}^+$, and 7.5 Å for $\mathbf{3}^+$, using $V_H = (0.0206/d)(E_{op}\,\epsilon_{max}\Delta\nu_{1/2})^{1/2}$.[16] [b] In kcal/mol. Calculated using the quartic fit; negligibly different from $\Delta G^* = (\lambda/4)(1 + C/4)/(1 + C) - V_H + V_H^2/\lambda$.[16] [c] In s^{-1}. Calculated from eq 6 using $\lambda_v = 25$ kcal mol^{-1} for $\mathbf{1}^+$ and $\mathbf{2}^+$, and 20 kcal mol^{-1} for $\mathbf{3}^+$, and $h\nu_v = 800$ cm^{-1}.[16] [d] In kcal mol^{-1}, using $\Delta G^*(IP) = \Delta G^*(1 + \Delta G°_{ET,IP}/[4\Delta G^*])^2$. [e] Calculated using eq 6, replacing ΔG^* by $\Delta G^*(IP)$.

TABLE 4: Optical Predictions of Rate Constants for Thermal ET of $\mathbf{2}^+PF_6^-$ at 293 K with Ion Pairing

	method A[a]	method B[b]	method C[c]
$\Delta G°_{ET}$ (kcal/mol)	2.6	2.1	0.0
λ (kcal/mol)	37.2	37.1	39.3
C	0.11	0.11	0.09
$\Delta\nu_{1/2}$ (cm^{-1})	6270	6200	6280
ϵ (M^{-1} cm^{-1})	2650	2680	2680
V_H (kcal/mol)	3.44	3.42[2.87][d]	3.54[2.97]
ΔG^* (kcal/mol)	6.82	6.56[7.02]	6.00[6.47]
k_{OPT} (10^8 s^{-1})	1.61	2.53[1.15]	6.44[2.85]
$k_{OPT}/k_{ESR}(293)$	0.81	1.27[0.58]	3.24[1.43]

[a] Assuming no change in ET parameters from free $\mathbf{2}^+$, but the ET is endothermic by $E_{op}^{IP} - E_{op}^{free}$. The spectrum used contained 26 mM $\mathbf{2}^+PF_6^-$ and no added salt. [b] Assuming the observed optical band represents an ET that is endothermic by $E_{op} - E_{op}^{free}$. The spectrum used contained 37 mM $\mathbf{2}^+PF_6^-$ and 32.4 mM $^nBu_4NPF_6$. [c] Setting $\Delta G° = 0$ for analysis of the same optical spectrum as for b. [d] The numbers in brackets use $V = V_H/(n)^{1/2}$.

The photo-ET process revealed in the absorption spectrum is very rapid, converting the initial system (ion paired at the initially positive hydrazine unit) to a final one that is not ion paired at its positive hydrazine unit, which is clearly an endothermic process. The smallest concentration available for analysis of optical data for $\mathbf{2}^+PF_6^-$ in methylene chloride was 0.026_5 mM. This solution had $\lambda_{max} = 769$ nm, corresponding to $E_{op} = 49$ cm^{-1} (0.14 kcal/mol) higher than the E_{op}^{free} obtained from the fit of Figure 1b, and about 7% ion pairing based on $K_{IP} = 3100$ M^{-1}. This spectrum was therefore simulated with $\Delta G°_{ET,IP} = 0.14$ kcal/mol, and produced the ET parameters shown in Table 3, along with data for the other two compounds determined in the same manner. We note that C, even in the absence of ion pairing, is larger in methylene chloride than in acetonitrile for all three compounds. Larger C in methylene chloride than in acetonitrile has also been observed for all other compounds studied,[16,21] although the solutions previously studied were significantly ion paired in methylene chloride. C presumably increases in such solutions because the band observed is the superposition of ion-paired and non-ion-paired spectra at different E_{op} values. For example, the spectrum previously published for $\mathbf{1}^+$ in methylene chloride had $E_{op} = 12\,630$ cm^{-1},[16a] 0.76 kcal/mol larger than E_{op}^{free}, indicating significant ion pairing, and showed a detectably larger C value (0.275) than the value of 0.24 estimated for the free ion (Table 3). Table 3 contains k_{OPT} values for the free ions calculated using the same equation employed previously, eq 6.[16] We also estimated k_{OPT}

$$k_{ET} = \nu_v (\lambda_v/\lambda)^{1/2} \exp(-\Delta G^*/RT) \qquad (6)$$

for the ion paired system from the ET parameters obtained for the free ion by assuming that ET process is endothermic by $\Delta G°_{ET,IP}$. We will call this method A for estimating an ion pairing effect. We replaced ΔG^* in the equation used for calculating k_{ET} for free ions, eq 6, by the quantity $\Delta G^*(IP) = \Delta G^*(1 + \Delta G°_{ET,IP}/4\Delta G^*)^2$, and left the other parameters unchanged. These values are listed in Table 3. The rate ratios in the absence to the presence of ion pairing using method A are 5.8, 9.9, and 14.6 for $\mathbf{1}^+$−$\mathbf{3}^+$ respectively. If these values were correct, the rate ratio for the "partially ion paired" to the "fully ion paired" k_{ESR} values ought to be larger than the 1.6 observed for $\mathbf{2}^+PF_6^-$. The other ET parameters may well not remain constant as ion pairing occurs, of course, so method A estimates may not be very accurate.

In Table 4 we compare the Method A IV−CT band fitting parameters and resulting k_{OPT} values for $\mathbf{2}^+PF_6^-$ with two other methods for estimating $k_{OPT}(IP)$ for which instead of using the least ion-paired spectrum we could obtain, employ the most ion-paired spectrum. The optical spectrum was determined for 37 mM $\mathbf{2}^+PF_6^-$ in the presence of 32.4 mM $^nBu_4NPF_6$, so this spectrum corresponds to a very high fraction of ion pairing. For method B, we use $\Delta G°_{ET,IP} = E_{op}(\text{obsvd}) - E_{op}^{free} = 2.1$ kcal/mol (instead of using the method A extrapolated values,

($E_{op}^{IP} - E_{op}^{free}$) = 2.5 kcal/mol) in fitting the spectrum observed at high concentration with added salt. The ϵ_{max} obtained was only slightly higher, and the λ, C, and $\Delta\nu_{1/2}$ are quite similar to those obtained from the low concentration, no added salt spectrum (the method A column). The method B k_{OPT} value is slightly (a factor of 1.57) larger than that obtained using method A.

In method C, we analyze the same high concentration, salt-added spectrum as for method B, but use $\Delta G° = 0$. Thermal ET for an ion-paired system requires electron transfer, solvent reorganization, and counterion transfer. The first two of these processes must occur even in the absence of ion pairing. Both solvent and internal vibrational reorganization energy are included in a "merged" ET coordinate, and photo-ET reveals the adiabatic surface on which the ET occurs, including both processes. It appears possible that the effect of ion pairing might be absorbed into the ET coordinate along with the solvent and internal vibrational effects. Indeed, as pointed out earlier, method C analysis, setting $\Delta G° = 0$, appeared to allow accurate prediction of rate constants both for aromatic-bridged intervalence bis(hydrazines)[16] and for saturated bridged bis(hydrazines) and bis(diazeniums),[21,22] some in acetonitrile (where ion pairing effects are negligible) and some in methylene chloride (where they are easily detectable, as shown in this work). As shown in the method C column of Table 4, fitting the ion-paired spectrum with $\Delta G° = 0$ results in a larger λ, slightly larger V, slightly smaller C, and increased the k_{OPT} obtained by a factor of 2.5, not a very large change.

As shown graphically in Figure 3, using Methods A and B (positive $\Delta G°_{ET,IP}$ caused by the ion pairing) gives a better fit to the ESR rate data for $\mathbf{2}^+BF_4^-$, but it must be noted that this occurs because V_H values quoted were used, and that evaluating V includes assumptions that may not be true. In obtaining V_H, we used a modeled ET distance (8 Å)[16a] whose applicability is arguable, and have not included a refractive index (n) correction to V. A refractive index correction would lower V by a factor of 0.84 (using $V(\text{corrected}) = V_H/(n)^{1/2}$) or 0.89 (using the correction factor introduced by Chacko).[16b] The effective n in solvent containing added salts may also be different from that of the pure solvent. Using the largest n correction in calculating V brings the method C k_{OPT} value into closer agreement with k_{ESR} than the method A and B values, as indicated by the numbers in brackets in Table 4. The most important feature of Table 4 is that methods B and C predict k_{OPT} values that differ only by a factor of 2.5, rationalizing the good agreement of k_{OPT} with k_{ESR} obtained in previous work,[16,21,22] where $\Delta G = 0$ was used for band analysis even for partially ion paired solutions (that is, method C was used). Because the solutions examined were near 1 mM and did not have added salt, they were clearly less ion paired than that used for method C of Table 4 and Figure 3, and the difference between a method C treatment and one in which the ion pairing is accounted for using method B would be smaller. We note that the simplest treatment (method C), lumping the ion pairing effect into the ET coordinate along with the vertical vibrational and solvent reorganization leads to results that would only be distinguishable from explicitly including a nonzero driving force for optical ET if this driving force, as well as all of the other ET parameters, were rather accurately known. We do not include detailed comparisons of k_{OPT} with k_{ESR} for the rate data for $\mathbf{1}^+PF_6^-$ or $\mathbf{3}^+NO_3^-$ here. Agreement is good, but the ESR rate constants are only available at lower temperatures than those for the optical spectra, and temperature extrapolation errors are large enough not to provide additional insight into the best way to analyze the data.

Conclusions

This work demonstrates that bis(hydrazine) cations are significantly ion paired in methylene chloride, and that the effect of ion pairing on E_{op} is easily detectable. The K_{IP} values determined from the effect of concentration on the IV−CT band position indicate that cation structure is not very important in determining K_{IP}, and that $\Delta G°_{ET,IP}$ is significantly smaller than $\Delta G°_{IP}$, so the effect of ion pairing on k_{ET} is not very large. Calculating k_{OPT} for a very highly ion-paired solution of $\mathbf{2}^+PF_6^-$ by fitting the observed IV−CT band with $\Delta G° = 0$ instead of including a $\Delta G° > 0$ ion pairing effect only resulted in k_{OPT} being a factor of 2.5 larger. Uncertainty in the proper ET distance to use and possible refractive index correction in calculating V from the optical spectrum leads to uncertainty in k_{OPT} that are comparable to this difference.

Intervalence compounds can serve as sensors for the concentration of free counterion in a solution, by use of eq 1. We know of no other way of determining $[\mathbf{X}^-]$ in a solution containing a mixture of cations. The compounds studied here are far from being optimized to maximize ΔE_{op} (optimized compounds would have $\Delta G°_{ET,IP}$ as close to $-\Delta G°_{IP}$ and as large as possible), which would be desirable for development of useful $[\mathbf{X}^-]$ sensors.

Experimental Section

The compounds used[16b] as well as ESR and optical data collection and treatment are as previously described.[16] The Mathematica package was used for calculations involving fits to eq 3, 4, and 5.

Acknowledgment. We thank the National Science Foundation for support of parts of this work under grant CHE-9417946, the NSF major instrument program and the University of Wisconsin for funds used in purchase of the spectrometers and computer equipment used, and the Dow Chemical Company for a fellowship for R.F.I. We thank Jeff Curtis (University San Francisco) for valuable discussions.

References and Notes

(1) *Ions and Ion Pairs in Organic Reactions*; Szwarc, M., Ed.; Wiley-Interscience: New York, 1972 (Vol. 1), 1974 (Vol. 2).

(2) Schlitzer, D. S.; Novak, B. M. *J. Am. Chem. Soc.* **1998**, *120*, 2196.

(3) Corey, E. J.; Xu, F.; Noe, M. C. *J. Am. Chem. Soc.* **1997**, *119*, 12414.

(4) Kratochvil, B.; Yeager, H. L. *Topics Curr. Chem.* **1972**, *25*, 1−58.

(5) (a) Darensbourg, M. Y. *Prog. Inorg. Chem.* **1985**, *33*, 221−74. (b) Ashby, E. C.; Dobbs, F. R.; Hopkins, H. P., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 2823.

(6) (a) Pochapsky, T. C.; Stone, P. M. *J. Am. Chem. Soc.* **1990**, *112*, 6714. (b) Pochapsky, T. C.; Stone, P. M.; Pochapsky, S. S. *J. Am. Chem. Soc.* **1991**, *113*, 1460. (c) Koska, N. A.; Wilson, S. R.; Schuster, G. B. *J. Am. Chem. Soc.* **1993**, *115*, 11628.

(7) (a) Sutin, N. *Progr. Inorg. Chem.* **1983**, *30*, 441. (b) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

(8) Chen, P.; Meyer, T. J. *Chem. Rev.* **1998**, *98*, 1439.

(9) Piotrowiak, P.; Miller, J. R. *J. Phys. Chem.* **1993**, *97*, 13052.

(10) (a) Yang, E. S.; Chan, M.-S.; Wahl, A. C. *J. Phys. Chem.* **1980**, *84*, 3094. (b) Wherland, S. *Coord. Chem. Rev.* **1993**, *123*, 169.

(11) (a) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1. (b) Crutchley, R. J. *Adv. Inorg. Chem.* **1994**, *41*, 273.

(12) (a) Lewis, N. A.; Obeng, Y. S. *J. Am. Chem. Soc.* **1988**, *110*, 2306. (b) Lewis, N. A.; Obeng, Y. S.; Purcell, W. L. *Inorg. Chem.* **1989**, *28*, 3796. (c) (a) Lewis, N. A.; Obeng, Y. S. *J. Am. Chem. Soc.* **1989**, *111*, 7624.

(13) Lowery, M. D.; Hammack, N. S.; Drickhamer, H. G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 8019.

(14) (a) Blackbourn, R. L.; Hupp, J. T. *Chem. Phys. Lett.* **1988**, *150*, 399. (b) Blackbourn, R. L.; Hupp, J. T. *J. Phys. Chem.* **1990**, *94*, 1788.

(15) Blackbourn, R. L.; Dong, Y.; Lyon, D. L.; Hupp, J. T. *Inorg. Chem.* **1994**, *33*, 4446.

(16) (a) Nelsen, S. F.; Ismagilov, R. F.; Powell, D. R. *J. Am. Chem. Soc.* **1997**, *119*, 10213. (b) Nelsen, S. F.; Ismagilov, R. F.; Gentile, K.; Powell, D. R. Submitted for publication.

(17) Warner, L. W.; Hoq, M. F.; Myser, T. K.; Henderson, W. W.; Shepherd, R. E. *Inorg. Chem.* **1986**, *25*, 1911.

(18) We did not observe significant deviation from the behavior calculated for a simple ion pairing equilibrium for $\mathbf{1}^+$−$\mathbf{3}^+$ in the concentration range studied (to ∼9, 5, and 1 mM, respectively). Blackbourn and Hupp report that their data for biferrocenium in methylene chloride do not fit a simple ion pairing equilibrium.[14] There are unfortunate mistakes both in the equation they used (instead of eq 1) and in distinguishing [$\mathbf{X}^-$] from [$\mathbf{X}^{\text{tot}}$], and they went to much higher concentrations of added salt and plotted both dilution and added salt experiments together. It is not clear that their conclusion is correct.

(19) A referee requested an Eigen−Fuoss estimate of K_{IP} for our systems. The Eigen−Fuoss equation (ref 7a, eq 9; ref 8, eq 4) considers dielectric continuum theory for two equal-sized touching spheres at a centers distance d (so its quantitative applicability to our compounds is not clear). At zero ionic strength (intended to estimate K_{IP}), the Eigen−Fuoss association constant (K_{a}) for species having charges z_1 and z_2 may be written $K_{\text{a}} = K_{\text{o}} \exp(-w/RT)$, where $K_{\text{o}} = 4\pi \text{N}_{\text{L}} d^3/3000$ [d is in cm^{-1}, $N_{\text{L}} = 6.022 \times 10^{23}$], and $w = z_1 z_2 e^2/(\epsilon_{\text{S}}\ d)$[$\epsilon_{\text{S}}$ is the dielectric constant of the solvent, 8.9 for methylene chloride]. Values of K_{a} of 6800 to 3300 (in the range observed for K_{IP}) are produced for d values between 7 and 8 Å.

(20) Bhattacharyya, D. N.; Lee, C. L.; Smid, J.; Szwarc, M. *J. Phys. Chem.* **1965**, *69*, 208.

(21) (a) Nelsen, S. F.; Ramm, M. T.; Wolff, J. J.; Powell, D. R. *J. Am. Chem. Soc.* **1997**, *119*, 6863. Nelsen, S. F.; Trieber, D. A., II; Wolff, J. J.; Powell, D. R.; Rogers-Crowley, S. *J. Am. Chem. Soc.* **1997**, *119*, 6873.

(22) Nelsen, S. F.; Ismagilov, R. F.; Trieber, D. W., II. *Science* **1997**, *278*, 846.