For these reasons, the interaction energy expressed as the sum $\Delta E_{HF} + \Delta E_{MP}^{(2)}$ is expected to better characterize H-bonding than is $\Delta E_{HF} + \epsilon_{disp}^{(20)}$. For purposes of improving the orientation dependence of the HF + D potential, addition of the $\epsilon_{es}^{(12)}$ term may be recommended. A simple analytical potential for the $\epsilon_{disp}^{(20)}$ term is proposed in this paper; a multipole expansion, preferably of distributed type,[46] could be used for $\epsilon_{es}^{(12)}$, incorporating the Hartree–Fock moments and their second-order MP correlation corrections.[15] However, the $\Delta E_{HF} + \epsilon_{disp}^{(20)} + \epsilon_{es}^{(12)}$ potential does not lead to improvement over HF + D in the sense that both underestimate the equilibrium distance. However, the book is not yet closed on $\epsilon_{es}^{(12)}$. Latest studies[47] show that orbital relaxation leads to a lowering of the $\epsilon_{es}^{(12)}$ term by 30% in the asymptotic region. More work on this subject in ongoing in this laboratory.

Weaknesses of various water–water potentials to properly describe the bulk properties of water are often attributed to nonadditive effects.[48] While this is no doubt true to some extent, a perhaps larger source of error may reside in the pairwise potential. For example, the most popular ab initio based potentials

such as MCY[49] and that of Clementi and Habitz[50] are based upon BSSE-uncorrected energies. On the other hand, a number of mixed "effective" and ab initio potentials such as those discussed in ref 14 approximate the total correlation correction to the interaction energy by dispersion energy alone. Failure to include other terms leads to an overestimate of the correlation energy as well as distortion of the anisotropy of the surface.

A reexamination of ab initio two-body water–water potentials may be warranted at this point. Our results lend strong support to the contention that the sum of $\Delta E_{HF} + \Delta E_{MP}^{(2)}$ represents a balanced view of H-bonding between H_2O molecules, including the most important correlation corrections to the interaction energy with respect to magnitude as well as anisotropy. Such a model is an economical vehicle that allows for calculation of the large number of geometrical configurations that need to be examined for the purpose of deriving an analytical potential.

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Does Marcus–Hush Theory Really Work? Optical Studies of Intervalence Transfer in Acetylene-Bridged Biferrocene Monocation at Infinite Dilution and at Finite Ionic Strengths

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Intervalence charge-transfer data for acetylene-bridged biferrocene monocation (Bf^+) have been collected in five solvents in the presence and absence of excess electrolyte and in the limit of infinite chromophore dilution. The study was motivated by earlier work which demonstrated that the intervalence absorption maximum for Bf^+ in methylene chloride could vary substantially with both chromophore concentration and added electrolyte concentration. In the present study similar (but smaller) variations are found in other solvents. The variations are ascribable to both ion pairing and higher order ionic association. For the available solvents the logarithms of the Bf^+X^- pairing constant ($X^- = PF_6^-$, BF_4^-, or ClO_4^-) is found to vary inversely with the solvent's static dielectric constant, D_s. When the ion-pairing effects are eliminated by dilution, a genuine test of the Marcus–Hush prediction of the solvent dependence of the intervalence charge-transfer energy (E_{op}^{MMCT}) is possible. For highly polar solvents ($D_s \geq 20$) a good fit of E_{op}^{MMCT} to $1/D_{op} - 1/D_s$ is found (where D_{op} is the optical dielectric constant and $1/D_{op}$ is the main variant in the two-term dielectric parameter). For methylene chloride, however, E_{op}^{MMCT} falls well below the best-fit line for five other solvents. The deviation is tentatively attributed to dielectric saturation and is expected, therefore, to be manifest in other media possessing limited dielectric strength. In light of these findings, a speculative interpretation of pressure-induced solvent freezing effects is offered. It is suggested that, in frozen CD_3CN, E_{op}^{MMCT} is simultaneously subjected to ion-pairing perturbations and to dielectric saturation effects and that the effects act in an offsetting, largely compensatory fashion. The speculation is supported by semiquantitative extrapolations from known liquid solvent behavior and by an analysis of intervalence bandwidths.

Introduction

One of the notable characteristics of research in the area of electron-transfer (ET) chemistry has been the long and sustained history of lively interplay between experiment and theory.[1,2] Bond reorganization effects, the Marcus "inverted region", and dis-

tance-dependent electron tunneling come to mind as examples of now well-established phenomena whose eventual acceptance was alternatively driven by elegant experimentation and insightful theoretical suggestions.[3] Yet another important concept, solvent reorganization, resisted verification for many years but was finally

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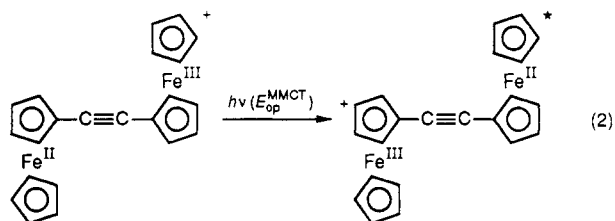
proven (or so it seemed) by optical intervalence methods.[4] Recently, however, the fundamental validity of the solvent reorganization concept, at least for intramolecular ET reactions, has been called into question (see eq 1).[5,6] If this criticism were to prove correct, it would likely necessitate a complete rethinking of the role of solvent in ET reactions, as well as the assembly of a new theoretical construct.

To elaborate, the solvent reorganization idea in its most primitive form assumes spatially separated reactants, spherical charge-trapping sites, a dielectric continuum for the solvent, and the occurrence of a "nonequilibrium polarization" of the solvent during an electron-transfer event.[7,8] As suggested by the Marcus–Hush expression

$$\chi_s = e^2(1/r - 1/d)(1/D_{op} - 1/D_s) \tag{1}$$

this leads to a number of simple predictions about the way in which the solvent reorganization energy (χ_s) should depend upon reactant and medium properties. In eq 1, e is the unit electronic charge, r the trapping-site radius, d the distance between sites (center-to-center), D_{op} the optical dielectric constant of solvent, and D_s the static dielectric constant of solvent.

Historically, the key to testing eq 1 was the recognition that χ_s would likely be the only size- and solvent-dependent component of the directly measurable intervalence (or metal-to-metal) charge-transfer absorption energy, E_{op}^{MMCT} (cf. eq 2). From eq

3, the other components are the inner-shell or vibrational reorganization energy (χ_i), the free energy difference (ΔE) between vibrationally and electronically relaxed initial and final states, and a quantity ($\Delta E'$) describing any additional electronic energy associated with excitation to a spin–orbit or ligand-field excited state.[8] The catalyst that eventually led to the direct evaluation
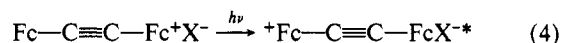
$$E_{op}^{MMCT} = \chi_s + \chi_i + \Delta E + \Delta E' \tag{3}$$

of eqs 1 and 3 by optical intervalence measurements was the synthesis in 1969 of solution-based dinuclear mixed-valence complexes.[9,10] The solvent dependence ($E_{op}^{MMCT} \propto (1/D_{op} - 1/D_s)$) was verified by Tom et al. in 1974,[4b] the distance dependence by Powers and Meyer in 1976,[11] the dependence on ΔE by Goldsby and Meyer in 1984,[12] and the dependence on $\Delta E'$ by Kober et al. in 1983.[13] It should be noted, however, that while the correct functional trends have usually been obtained, eqs 1 and 3 commonly fail to deliver values for E_{op}^{MMCT}, and especially χ_s, that are in satisfactory agreement with experiment.[4] A number of explanations have been considered, with most focusing on dielectric

cavity models in place of the so-called "conducting sphere model" implicit in eq 2.[14] At least one recent paper has also emphasized the possible significance of solvent "molecularity" effects in intervalence transfer reactions.[15] The important point, however, is that all of these models lead to the same or nearly the same *qualitative* predictions as eq 1, regarding variations in E_{op}^{MMCT} with solvent and so on.

The recent assertions that the solvent reorganization concept and especially the dielectric continuum model (eq 3) are incomplete or incorrect have been motivated by a variety of compelling new experimental results. First, E_{op}^{MMCT} has been found in several instances to depend on both the mixed-valence chromophore concentration and the concentration of added electrolyte.[5a,b,6,16] Neither result is expected superficially from eq 1. Second, when D_s (but not D_{op}) is decreased drastically (ca. 10-fold) by pressure-induced freezing, E_{op}^{MMCT} fails to respond or at best decreases by only a small amount.[5a,c] Again, this is contrary to the simplest interpretation of eq 1. Furthermore, as Hammack and co-workers have pointed out,[5a] in nearly all previous cases where eq 1 has been (seemingly successfully) put to the test, only the D_{op} term has been significantly varied. In other words, apart from very recent work, the dependence on D_s has not been satisfactorily examined. Third, in at least two cases involving strong ligand–solvent hydrogen bonding (HB), χ has been shown to vary with solvent HB parameters rather than with dielectric parameters.[6c,d] It should be noted, however, that not all systems displaying strong hydrogen bonding conform to this trend.[17]

In this report we address only the first two observations; the third we hope eventually to discuss elsewhere. The first observation—that E_{op}^{MMCT} increases with increasing ionic strength—has been linked by most investigators to ion pair (or ion aggregate) formation.[5,6,16] One possibility is that, for an ion pair, an extra reorganizational component exists due to counterion translation. We have shown, however, that the increase in intervalence transfer energy most probably arises from an ion-induced displacement of initial- and final-state zero-point energies,[16] a conclusion reached also by Lowery et al.[5b] This displacement, of course, is just the ΔE term already contained in eq 3 (albeit, in an unusual form), and in that sense the dielectric continuum treatment should *not* be judged insufficient. We note further that the origin physically for the ΔE term is in the ion-pairing-induced structural inequivalence of the MMCT reactant and initially formed photoproduct, e.g.

$$Fc—C{\equiv}C—Fc^+X^- \xrightarrow{h\nu} {}^+Fc—C{\equiv}C—FcX^{-*} \tag{4}$$

where Fc is ferrocene. Although this interpretation "explains" the experimentally observed ionic strength effects, it does not really answer the question posed by the title. It does show, however, that any meaningful tests of eq 2 will need to be made in the limit of infinite dilution.[18,19]

In the specific case of reaction 4 with $X^- = PF_6^-$ and methylene chloride as solvent, we have previously shown[16] that correction of E_{op}^{MMCT} for both ion pairing and higher order aggregation leads to a red shift of nearly 2000 cm^{-1}. In our earlier report, a comparison of the corrected value to the absolute energy predicted by eq 3 (with ΔE and $\Delta E'$ equal to zero) did not lead to particularly close agreement. Furthermore, as various workers have pointed out,[5a,6a] the ion-pairing-induced variations in E_{op}^{MMCT} in a *single* solvent can sometimes equal or even exceed those claimed in the literature for a full collection of solvents. There is good reason, then, to question whether eq 1 has really been validated by solvent-dependence studies.

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(17) Hupp, J. T.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 2332.

(18) As we shall see, as a practical matter "infinite dilution" can often be reasonably approximated by the millimolar concentrations typically employed in intervalence charge-transfer experiments.
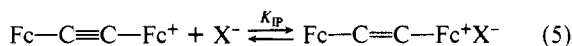
(19) Hammack and co-workers[5a,b] along with Lewis and Obeng[6a] have made similar points.

TABLE I: Solvent Dependent Intervalence Energies and Bandwidths for Acetylene-Bridged Biferrocene at Infinite Dilution

solvent	D_{op}	$D_s{}^a$	$1/D_{op} - 1/D_s$	E_{op}^{MMCT}, cm^{-1}	$\Delta\bar{\nu}_{1/2}$(exp), cm^{-1}	$\Delta\bar{\nu}_{1/2}$(calc),^{c} cm^{-1}
acetonitrile-d_3	1.807	37.5	0.526	7350	4000^d	4120
acetone-d_6	1.841	20.7	0.496	7350	4100^d	4120
nitromethane-d_3	1.909	38.6	0.498	7000	4100^e	4020
benzonitrile	2.338	25.2	0.388	6340	4150^f	3820
nitrobenzene-d_5	2.403	34.8	0.384	6250	4250^f	3800
methylene-d_2 chloride	2.022	9.1	0.380	4760	4400^d	3300
acetonitrile-$d_3{}^j$	(1.81)^g	43.3^h	(0.529)^g	~7500^i	~3300^{d,i}	
acetonitrile-$d_3{}^k$	(2.1)^g	3.9^h	(0.22)^g	~5650^i	~2450^{d,i}	

^{a} Taken from: *CRC Handbook of Chemistry and Physics*; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1984. ^{b} Values obtained at or near infinite dilution, except as noted. ^{c} Calculated by using eq 6. ^{d} Full width at half-height. ^{e} Obtained by doubling the bandwidth on the low-energy side. ^{f} Obtained by doubling the bandwidth on the high-energy side. ^{g} Estimated value; see ref 5a. ^{h} Taken from ref 5c. ^{i} For 2.3 mM Bf$^+$I$_3^-$. Taken from Figure 1 of ref 5c. $^j P = 1$ kbar; liquid. $^k P = 5.5$ kbar; solid.

Our goal in this study was to examine, in several solvents, intervalence transfer both with (eq 4) and without (eq 2) ionic association and to use the data to evaluate eqs 1 and 3 on a more completely defined experimental basis. We also wanted to quantitate the ion-pairing relation (eq 5) which links eqs 2 and

$$\text{Fc—C} \equiv \text{C—Fc}^+ + \text{X}^- \xrightarrow{K_{IP}} \text{Fc—C} = \text{C—Fc}^+\text{X}^- \qquad (5)$$

4, the purpose being to provide some measure of predictability regarding ionic strength effects. The experiments have been reasonably successful, and the combination of results has permitted us to speculate on the remarkable findings in the earlier solvent-freezing experiments.[5a,c] Our target system in all experiments was the acetylene-bridged biferrocene monocation (Bf$^+$). The choice was motivated by (1) the existence of data from our own lab[16] and elsewhere[5] which indicated that ion-association effects upon intervalence transfer energetics could be successfully (i.e., quantitatively) evaluated, (2) the observation that the chromophore fulfills the structural requirements ($2r < d$) prescribed by Marcus[7] for application of eq 1, (3) the realization that the transition dipole moment for metal-to-metal charge transfer must be relatively large if eq 1 is to display large solvent effects, and (4) the observation that the valence trapping sites in Bf$^+$ are strongly localized, yet sufficiently interactive, to yield good intervalence oscillator strengths.[20] Point 3, in particular, has not always been appreciated in previous work.

Experimental Section

Materials. The neutral acetylene-bridged ferrocene dimer was obtained from Dr. B. Patrick Sullivan. (A synthesis has been given by Rosenblum et al.[21]) The mixed-valence compound was obtained as a solid hexafluorophosphate salt by oxidation in toluene with p-benzoquinone, following the method of Dong et al.[22] Tetrabutylammonium hexafluorophosphate (TBAH) and tetrabutylammonium tetrafluoroborate (TBAB) were prepared and purified as outlined by Sawyer and Roberts.[23] Deuterated methylene chloride, deuterated acetonitrile, deuterated acetone, deuterated nitromethane, deuterated pyridine, deuterated dimethyl sulfoxide, benzonitrile (HPLC grade), propylene carbonate (99+%), tetramethylurea (99%), and 1-methyl-2-pyrrolidinone (HPLC grade) were all purchased from Aldrich. The first seven were used as received. The last three were used after passage (under dry nitrogen) through a column of activated alumina. Deuterated solvents were used, where possible, in order to gain transparency in the near-IR.

Measurements. Intervalence absorption bands were obtained by using 1-, 4-, and 10-cm matched cells in a Perkin-Elmer 330 UV–vis–near-IR spectrophotometer and an OLIS modified Cary-14 UV–vis–near-IR spectrophotometer. The measurements were ultimately limited by the onset of solvent absorption and/or quartz absorption at $E < 4700$ cm^{-1}. Values of E_{op}^{MMCT} could be
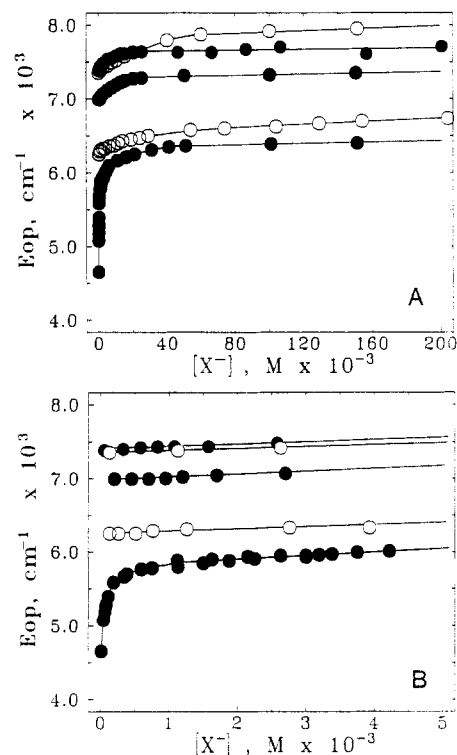
(20) Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 4393.

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(22) Dong, T. Y.; Kambara, T.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1986**, *108*, 4423.

(23) Sawyer, D. T.; Roberts, J. L. *Experimental Electrochemistry for Chemists*; Wiley: New York, 1984.

Figure 1. Metal-to-metal charge-transfer energy versus total anion concentration for the mixed-valence chromophore Fc—C≡C—Fc$^+$ in several solvents: (A) full scale, (B) expanded concentration scale. Key to solvents and electrolytes (from top): (O) acetonitrile-d_3 + TBA$^+$BF$_4^-$, (●) acetone-d_6 + TBA$^+$PF$_6^-$, (●) nitromethane-d_3 + TBA$^+$PF$_6^-$, (O) nitrobenzene-d_5 + TBA$^+$BF$_4^-$, and (●) methylene-d_2 chloride + TBA$^+$-PF$_6^-$.

determined reproducibly to within 60 cm^{-1}. For each solvent, "infinite dilution" values were obtained by reducing the mixed-valence chromophore concentration until the intervalence band maximum displayed no further shift in energy. These limiting values for E_{op}^{MMCT} were typically obtained with chromophore concentrations of a few micromolar to several hundred micromolar. Once the limiting low concentrations were achieved, ionic association effects were evaluated by systematic addition of TBAH or TBAB.

Results

Intervalence Energies. Figure 1 shows E_{op}^{MMCT} values for the acetylene-bridged biferrocene cation versus total anion concentration (PF$_6^-$) in methylene chloride, nitrobenzene, acetone, nitromethane, and acetonitrile as solvent. (Similar results were obtained for ClO$_4^-$ and BF$_4^-$ counterions. These will be reported elsewhere, within the context of a discussion of ion-pairing effects upon ET kinetics.[24]) We also attempted unsuccessfully to collect

(24) Blackbourn, R. L.; Hupp, J. T. *J. Phys. Chem.*, submitted for publication.
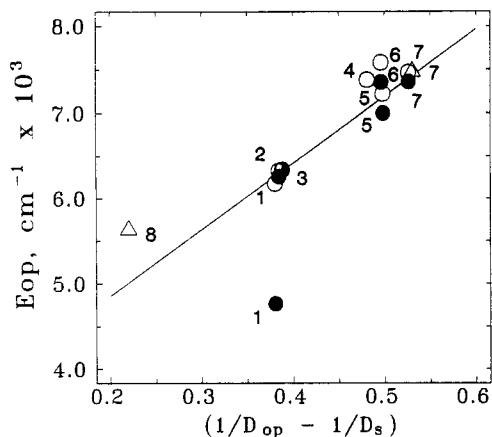
Figure 2. E_{op}^{MMCT} versus $(1/D_{op} - 1/D_s)$: open circles, $Bf^+PF_6^-$ at unspecified (ca. millimolar) concentrations (ref 20); triangles, 2.3 mM $Bf^+I_3^-$ (ref 5c); closed circles, $Bf^+PF_6^-$ at or near infinite dilution (current work). Key to solvents: (1) methylene chloride, (2) nitrobenzene, (3) benzonitrile, (4) propylene carbonate, (5) nitromethane, (6) acetone, (7) acetonitrile, (8) frozen acetonitrile ($T = 25$ °C, $P = 5.5$ kbar).

TABLE II: Ion-Pairing Equilibrium Constants for Bf^+X^- in Various Solvents

solvent	electrolyte	K_{IP}, M^{-1}	K_{IP}^{*b}
acetonitrile-d_3	$NaClO_4$	66	8
acetonitrile-d_3	$TBA^+BF_4^-$	40	9
acetone-d_6	$TBA^+BF_4^-$	180	6
acetone-d_6	$TBA^+PF_6^{-c}$	370	38
nitromethane-d_3	$TBA^+PF_6^-$	70	5
dichloromethane-d_2	$TBA^+PF_6^-$	9000[a]	31

[a] Activity corrections and electrolyte self-association effects neglected. [b] Estimated as described in text.

dilute-solution absorption spectra in pyridine-d_5, tetramethylurea, 1-methyl-2-pyrrolidinone, dimethyl-d_6 sulfoxide, and propylene carbonate. (We were able to obtain spectra at millimolar levels in propylene carbonate but not at submillimolar concentrations.) In most cases the reason for failure appeared to be either solvent-induced reduction or further chemical degradation of the mixed-valence ion. In those solvents where satisfactory data were obtained, values of E_{op}^{MMCT} at infinite dilution were taken from the intercepts in the anion concentration plots (Table I). The expanded plots in Figure 1b show that, with the exception of measurements in methylene chloride, limiting low-concentration values could be obtained without extrapolation.

Figure 2 (filled circles) shows a plot of the infinite-dilution E_{op}^{MMCT} values versus the dielectric parameter $(1/D_{op} - 1/D_s)$. Included for comparison (open circles) are data collected by Powers and Meyer at roughly millimolar concentrations.[20] Also included are points obtained by Hammack et al. for 2.3 mM $Bf^+I_3^-$ in liquid and frozen CD_3CN.[5c]

We have shown elsewhere that the shifts in charge-transfer energy with anion concentration are due (at least at low concentrations) to ion pairing (eq 5).[16] If the extinction coefficients for paired and unpaired chromophores are similar and if the spectra overlap, the ion-pairing constant (K_{IP}) can be obtained from the inverse slope of a plot of $\{\Delta E_{op}^{MMCT}(100\%)/[E_{op}^{MMCT} - E_{op}^{MMCT}(initial)] - 1\}$ versus $1/\gamma[X^-]$[25,26] (see Table II). In the plot, $\Delta E_{op}^{MMCT}(100\%)$ represents the difference in intervalence transition energy between the completely paired and completely unpaired complexes, while γ is the mean ionic activity coefficient for the added electrolyte. (γ values were obtained from the extended Debeye–Hückel equation with appropriate corrections for electrolyte self-association.[27]) Linear plots were obtained in

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

(26) Ion-pairing constants were obtained by a regression analysis which took into account (and appropriately weighted) varying uncertainties in the *y* direction. See: Taylor, J. R. *An Introduction to Error Analysis*; University Science Books: Mill Valley, CA, 1982.
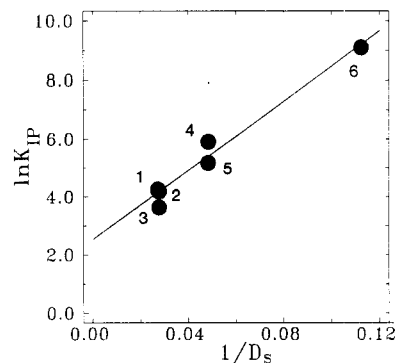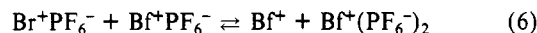
Figure 3. Plot of ln $K_{IP}(Bf^+X^-)$ versus $1/D_s$ in several solvents: (1) nitromethane, $X^- = PF_6^-$; (2) acetonitrile, $X^- = ClO_4^-$; (3) acetonitrile, $X = BF_4^-$; (4) acetone, $X^- = PF_6^-$; (5) acetone, $X^- = BF_4^-$; (6) methylene chloride, $X^- = PF_6^-$.

acetonitrile, nitromethane, and acetone. For nitrobenzene, however, the plot is decidedly nonlinear and K_{IP} cannot be obtained by this method.

The results in methylene chloride also deserve special mention. Here the ionic strength dependence is biphasic.[16] We previously ascribed the second equilibrium to ion tripling, and indeed this may be correct when the counterion source is chiefly the added electrolyte ($TBA^+PF_6^-$). When the chromophore and its counterion are exclusively present, however, ion tripling is possible only at the expense of ion pairing:

$$Br^+PF_6^- + Bf^+PF_6^- \rightleftharpoons Bf^+ + Bf^+(PF_6^-)_2 \qquad (6)$$

A consideration of the equilibrium constants shows that this process cannot occur to any significant extent. A more probable explanation is that the second equilibrium involves ion-pair aggregation. (i.e., $nBf^+PF_6^- \rightleftharpoons (Bf^+PF_6^-)_n$, where the overall aggregation could presumably occur by a succession of n individual steps).

Absorption Bandwidths. According to Hush,[8] the width of an intervalence absorption band ($\Delta\bar{\nu}_{1/2}$) can provide an independent measure of the reorganization energy (and vice versa). The predicted relation is

$$\Delta\bar{\nu}_{1/2} = [16(\ln 2)kT(\chi_s + \chi_i)]^{1/2} =$$
$$[16(\ln 2)kT(E_{op}^{MMCT} - \Delta E - \Delta E')]^{1/2} \qquad (7)$$

Table II lists values for $\Delta\bar{\nu}_{1/2}$ calculated from the right-hand side of eq 7. In the calculation, $\Delta E'$ was assumed to be negligible and ΔE was forced to zero by choosing E_{op}^{MMCT} values in the limit of infinite dilution. The corresponding experimental values (also at or near infinite dilution) are likewise collected in Table I.

One of the assumptions underlying eq 6, of course, is that only a single MMCT chromophore is present. If multiple chromophores are present (e.g., Bf^+ and Bf^+X^-), the overall observed intervalence envelope will contain multiple absorption bands and therefore will be broadened. If two individual bands have identical shapes and intensities, then the maximum apparent width will occur when the pair of chromophores is present at equal concentration. Behavior of this type has been reported by us previously.[16,24] In replicating those findings in the present study, the most notable observations were the systematic broadening and then narrowing of the intervalence band as the extent of ion pairing increased. Also significant is the observation that the maximum widths occurred near 50% ion pairing;[29] this provides an independent

(27) See, for example: Borchardt, D.; Wherland, S. *Inorg. Chem.* **1981**, *21*, 2537, and supplementary material for that article.

(28) It should be noted that the equilibrium constant listed in Table II for ion pairing in CD_2Cl_2 differs slightly from that reported in ref 16, even though the same experimental data were employed. The difference comes from a revised value for E_{op}^{MMCT}(initial)[26] and therefore, $\Delta E_{op}^{MMCT}(100\%)$. (The revised value for the former is 4760 cm⁻¹.) We previously relied upon a curved extrapolation to estimate E_{op}^{MMCT}(initial).[16] The evaluation can be linearized, however, by constructing a plot of $(\Delta E_{op}^{MMCT}(100\%)/[E_{op}^{MMCT} - E_{op}^{MMCT}(final)] - 1)$ versus $[X^-]$ and imposing the condition (by adjusting $\Delta E_{op}^{MMCT}(100\%)$) that the intercept equal zero.

validation of the above estimates of K_{IP}.

Discussion

Perhaps the most surprising finding in view of the previous work on both Bf^+ in dichloromethane and biferrocene monocation in nitrobenzene is just how *little* the new E_{op}^{MMCT} values[20] at infinite dilution differ from the published values obtained at ca. millimolar concentrations. The differences that do exist presumably are from residual amounts of ion pairing. Figure 2 confirms that, for most of the available solvents, ion pairing is indeed largely absent at $[X^-] \leq 1$ mM. It would be useful, nonetheless, to be able to predict just which solvents are likely to present ion-pairing problems at any given chromophore or chromophore-plus-electrolyte concentration. Obviously, that could be accomplished if one could predict the magnitudes of ion-pairing constants. Figure 3 shows that a useful (and potentially predictive) correlation does exist between $\ln K_{IP}$ and $1/D_s$. The correlation is expected, of course, if the differences in ionic association are due mainly to differences in Coulombic attraction.

Given the new results, we can begin (at least for this system) to address the question posed by the title: Does Marcus–Hush theory really work? Figure 2 demonstrates very clearly that when ion-pairing artifacts are absent, the energy for intervalence transfer in Bf^+ displays the expected dependence on $1/D_{op}$. (Note, however, that apart from CD_2Cl_2, frozen acetonitrile, and perhaps acetone as solvent, variations in the D_s term are negligible.) Admittedly, the plot shows nearly a 2-fold smaller slope than predicted by eq 1 (based on $r = 3.9$ Å and $d = 7.3$ Å (trans configuration)). As noted in the Introduction, however, this type of deviation is common in optical ET studies; elsewhere, numerous explanations have been presented[14,15,20] and discussed.[14,15] Since we have nothing new to contribute to that particular discussion, we will not reiterate the explanations.

Returning to the question of the dependence of E_{op}^{MMCT} on the static dielectric constant, Figure 2 suggests a mixed result. When D_s is decreased by freezing, the transition energy likewise decreases. Furthermore, the extent of the energy decrease is fairly close to what one would predict from the best-fit line (excluding methylene chloride)[30] to $1/D_{op} - 1/D_s$ (however, see later discussion). On the other hand, when D_s is substantially decreased by simply changing the identity of the liquid solvent (to CD_2Cl_2), there is an unexpectedly large decrease in energy. In other words, D_s behaves as if it were even smaller (and $1/D_s$ even larger) than its known value (ca. 9.1). The simplest interpretation (and the one which we favor) is that, in the presence of a charged chromophore like Bf^+, the solvent dielectric response is field saturated and the *local* dielectric strength is less than D_s.[31] At a microscopic level, the saturation effect might be attributed to a loss of librational or other degrees of freedom. This could arise from overly strict alignment of solvent dipoles by the electrical field created by the cationic charge. For higher dielectric strength solvents, one would expect the saturation effect to be absent, as seems to be the case. It should be noted that dielectric saturation has often been invoked to explain anomalies in redox processes involving complex ions. To our knowledge, however, this is the first reasonably compelling experimental evidence that, in ET reactions, saturation can exert a profound effect.

Given the apparently clear picture of optical ET in liquid solvents, it may be worthwhile speculating on the significance of data collected in frozen solvents. A point that has been emphasized

already is that when a solvent is subjected to pressure-induced freezing, D_s decreases, χ_s is predicted to decrease, and consequently E_{op}^{MMCT} should decrease if there are no other energy effects.[5a,c] Although the existing data (Figure 2) seem to confirm the predictions (at least approximately), we regard the agreement as fortuitous. Recall that the frozen solvent experiments were performed with 2.3 mM $Bf^+I_3^-$.[5c] At this concentration, the chromophore and its counterion would almost certainly be completely associated and a substantial blue shift in E_{op}^{MMCT} would be expected. If ion pairing were the only form of association, the magnitude of the shift would be $\Delta E_{op}^{MMCT} = -RT \ln K_{IP}^*/K_{IP}$, where K_{IP}^* describes the stability of the mixed-valence species having X^- in contact with neutral ferrocene (rhs, eq 4).[32] From the dielectric correlation in Figure 3, K_{IP} can be estimated as ca. 5×10^7 M^{-1}. Unfortunately, K_{IP}^* cannot be similarly estimated. It is worth noting, however, that a very rough empirical correlation exists between $\ln K_{IP}$ and $\ln K_{IP}^*$ for other solvents. Consequently, we find empirically that ΔE_{op}^{MMCT} also increases approximately with $\ln K_{IP}$. Extrapolating from the liquid solvents, ΔE_{op}^{MMCT} is estimated to be ca. 1900 cm^{-1} in frozen acetonitrile. Neglecting other factors, this would place the point for frozen CD_3CN well *above* the best-fit line in Figure 2.

From the current experiments with methylene chloride, the other major consequence of lowering the static dielectric constant would be the induction of dielectric saturation. In frozen acetonitrile this would have the effect of *lowering* E_{op}^{MMCT}. If the ion-pairing and dielectric saturation effects were precisely compensatory, the observed correlation in Figure 2 would result.

To test this hypothesis further, one would need an independent means for distinguishing the two effects. To this end, it is important to note that ion pairing will change E_{op}^{MMCT} chiefly through ΔE (eq 3)[32] but that dielectric saturation should exert an influence only through χ_s. One means of separating the effects would be to evaluate intervalence bandwidths, since these are expected to respond only to χ (provided that only one chromophore is present; see Results section). Table I shows that there is a substantial decrease in $\Delta\bar{\nu}_{1/2}$ (and by inference, χ) upon freezing the solvent. If the bandwidth is then employed to calculate just the reorganizational part of E_{op}^{MMCT} (eq 6), the value is ca. 2600 cm^{-1}. This can be compared with the overall (measured) E_{op}^{MMCT} value of 5650 cm^{-1} (Table I). On this basis, an energy deficit of about 3000 cm^{-1} exists. Recall, however, that the quantity $-RT \ln K_{IP}^*/K_{IP}$ should contribute an amount approaching the deficit, i.e., 1900 cm^{-1}. Thus, a compensatory energy effect appears almost certainly to exist.

Although the rough agreement between experiment and hypothesis is intriguing, the comparison entails some significant assumptions. First, ionic association is assumed to be limited to pairing interactions. If ion-pair aggregation also occurs (see Results section), then our estimate for ΔE_{op}^{MMCT} will be too small. On the other hand, chromophoric species within an aggregate might be environmentally isolated and therefore subject to much less solvent reorganization.[5b] Consequently, that component of E_{op}^{MMCT} would be expected to diminish. A second, more critical assumption is that the magnitude of χ is genuinely reflected by $\Delta\bar{\nu}_{1/2}$. Previous experimental comparisons to eq 6 have not been particularly convincing.[4,20] (The experimental values generally are "too large".) We have noted elsewhere[16] however, that most (perhaps all) previous studies are compromised by partial ion pairing. This leads to artificial band broadening and, therefore, to doubt concerning earlier conclusions about eq 6. The present experiments are largely free from such artifacts. With that in mind, the first five entries in Table I strongly suggest that eq 6, which relates $\Delta\nu_{1/2}$ to E_{op}^{MMCT} and therefore χ, is valid. Note that once ion pairing is eliminated there is near-quantitative agreement between calculated and observed bandwidths. Admittedly, the spread of values is small, so a trend is difficult to demonstrate (or repudiate). Also the sixth entry (CD_2Cl_2) is larger than predicted. Although it is tempting to ascribe this last result to

(29) Actually, in methylene chloride or acetone as solvent the maximum bandwidth occurred at values closer to 60–70% ion pairing. This could be indicative of a systematic error in the calculation of K_{IP}. (For example, E_{op}^{MMCT}(final) might be underestimated. In the acetone case, arbitrary adjustment of E_{op}^{MMCT}(final) to cause $\Delta\bar{\nu}_{1/2}$ to maximize at 50% ion pairing, leads to a value of 310 M^{-1} for K_{IP}.) An alternative explanation is that at higher electrolyte concentrations the band is artificially broadened by tailing from the visible region or by contributions from higher order ionic association.

(30) The point for CD_2Cl_2 lies more than 9σ below the best-fit line for the remaining solvents.

(31) A related explanation involving a frequency-dependent cation size has been suggested by McManis et al.[15] within the context of a mean spherical approximation.

(32) We assume here that the blue shift in liquid solvents comes only from a relative displacement of zero-point energies.

some unique (unknown) noncontinuum effect, a safer interpretation is that K_{IP} in CD_2Cl_2 is slightly underestimated. If this were true, then even at the very lowest available chromophore concentration (8×10^{-6} M) significant ion pairing would persist (and thereby broaden the absorption envelop). In principle, one could chek this by obtaining values for $\Delta\bar{\nu}_{1/2}$ at still lower concentrations. Unfortunately, 8×10^{-6} M appears to be a practical lower limit experimentally in this portion of the near-IR spectrum. Despite these uncertainties, however, we are inclined to accept eq 6 as a valid representation of the relation between $\Delta\bar{\nu}_{1/2}$ and χ when a single chromophore is present.

If the above interpretation of frozen-solvent phenomena is correct, it may be enlightening to consider briefly other examples. The two that are available in the literature are biferrocene monocation and $(bpy)_2ClRu^{II}(pz)Ru^{III}Cl(bpy)_2^{3+}$ (pz is pyrazine).[5a] These differ from Bf^+X^- in that almost no change in E_{op}^{MMCT} occurs upon pressure-induced freezing. Furthermore, $\Delta\bar{\nu}_{1/2}$ changes only slightly, if at all. Both observations would seem to signal a fundamental change in behavior in comparison to Bf^+X^-. There is a third observation, however, that may reconcile the results. From studies at millimolar concentrations in liquid solvents (where ion-pairing effects admittedly may exist), the variation of E_{op}^{MMCT} with $1/D_{op} - 1/D_s$ is (in both cases) exceedingly weak.[4c,20] This implies that χ_s is very small and further that χ_i will largely determine $\Delta\bar{\nu}_{1/2}$. It follows, then, that both the overall transition energy and the bandwidth will be comparatively insensitive to pressure-induced variations in D_s and χ_s.

Conclusions

The present results serve to reinforce and generalize our own previous findings[16] and others[5,6a] that ion pairing (and higher order ionic association) can influence the energies of intervalence transitions. Although ion-pairing effects are not treated in an explicit way by existing theories, they are implicit in redox asymmetry terms. In that sense, the dependence of E_{op}^{MMCT} on ionic strength is *not* contrary to dielectric continuum theory. Once ion-pairing effects are removed (by performing experiments at or near infinite dilution), the optical barrier to electron transfer within Bf^+ shows the expected inverse dependence on the optical dielectric constant. The "correct" dependence on D_s, however, is not found experimentally—a conclusion also reached by Hendrickson and co-workers.[5] One possible explanation is that dielectric saturation occurs in low-D_s solvents. A more appropriate expression then would be $E_{op}^{MMCT} \propto (1/D_{op} - 1/D_s(local))$. Although the revised expression differs materially from that suggested by Marcus–Hush theory, it should be noted that the revision was anticipated by Marcus and others in early formulations of the theory.[7]

Experiments in a frozen solvent (CD_3CN)[5c] appear to be complicated by both ion pairing and dielectric saturation. The effects apparently can be separated, however, by resort to bandwidth studies and quasi-empirical correlations between ΔE_{op}^{MMCT}, K_{IP}, and D_s. Because the effects act in opposite directions, energy compensation exists and E_{op}^{MMCT} approaches (fortuitously) the value predicted by simple extrapolation from the observed behavior in liquid solvents.

Molecular Structure and Conformation of Diisopropyl Ketone Studied by Gas Electron Diffraction Combined with Vibrational Spectroscopy and SCF MO Calculations[†]

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The molecular structure and conformation of diisopropyl ketone, $Me_2C(3)HC(2)OC(4)HMe_2$, at 24 °C have been investigated by gas electron diffraction with the aid of vibrational spectroscopy and ab initio SCF calculations at the 4-21G level. Three conformers with C_1, C_s, and C_2 symmetry exist with the molar fractions of 0.45 (31), 0.31 (12), and 0.24 (22), respectively. The dihedral angles $\phi_1(C_4C_2C_3H)$ and $\phi_2(C_3C_2C_4H)$ of the C_1, C_s, and C_2 conformers (the values are denoted by (ϕ_1, ϕ_2)) are (16°, -62°), (0°, 180°), and (59°, 59°), respectively, where ϕ_1 and ϕ_2 are defined to be zero when the C–C bond eclipses the C–H bond. The main structural parameters (r_g and $\angle_\alpha$) of the C_1 conformer with the limits of error (3σ) in parentheses are as follows: $r(C=O) = 1.215$ (5) Å, $\langle r(C—C) \rangle = 1.535$ (2) Å, $r(C—H) = 1.118$ (3) Å, $\angle CC(=O)C = 116.6$ (17)°, $\langle \angle CCC \rangle = 110.8$ (4)°, and $\angle CCH_{Me} = 111.1$ (9)°, where the symbol $\langle \ \rangle$ denotes average values.

Introduction

The conformations of diisopropyl ketone (DIK) have been investigated by several authors[1-3] with different conclusions. Aroney and co-workers[1] measured the molar Kerr constant of DIK in CCl_4 solution. They assumed the presence of two conformers, one in which both H_{i-Pr} atoms are anti to the oxygen atom (C_{2v} symmetry) and the other in which one H_{i-Pr} atom is syn to the oxygen atom and the other is anti to the oxygen atom (C_s symmetry). Here, H_{i-Pr} denotes the hydrogen atom attached to the tertiary carbon atom. By comparing the observed molar Kerr constant with the calculated ones, they inferred that the two conformers exist with the ratio of 1:2. Hirota and co-workers[2] measured the infrared spectra of DIK and related ketones in CCl_4 solution and concluded from the carbonyl stretching frequencies that the two H_{i-Pr} atoms of the predominant conformer of DIK are eclipsed with the oxygen atom (C_{2v} symmetry). Suter[3] developed a molecular mechanics force field for ketones and aldehydes and calculated the conformational energy of DIK. According to his calculation, the most stable conformer of DIK has C_2 symmetry with the dihedral angle,[4] $\phi_1(C_4C_2C_3H)$ ($=\phi_2$-

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(2) Hirota, M.; Hagiwara, T.; Satonaka, H. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2439.
(3) Suter, U. W. *J. Am. Chem. Soc.* **1979**, *101*, 6481.