For these reasons, the interaction energy expressed as the sum $\Delta E_{HF} + \Delta E_{MP}$ is expected to better characterize H-bonding than $\Delta E_{HF} + \Delta E_{MP}$. For purposes of improving the orientation dependence of the HF + D potential, addition of the $\Delta E_{MP}$ term may be recommended. A simple analytical potential for the $\Delta E_{MP}$ term is proposed in this paper; a multipole expansion, preferably of distributed type, could be used for $\Delta E_{MP}$, incorporating the Hartree–Fock moments and their second-order MP correlation corrections. However, the $\Delta E_{HF} + \Delta E_{MP} + \Delta E_{HF}$ 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 $\Delta E_{MP}$. Latest studies show that orbital relaxation leads to a lowering of the $\Delta E_{MP}$ term by 30% in the asymptotic region. More work on this subject is ongoing in this laboratory.

Weaknesses of various water–water potentials to properly describe the bulk properties of water are often attributed to non-additive effects. While this is not 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 and that of Clementi and Habitz 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 $\Delta E_{HF} + \Delta E_{MP}$ represents a balanced view of H-bonding between H2O 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 Intervalance Transfer in Acetylene-Bridged Biferrocene Monocation at Infinite Dilution and at Finite Ionic Strengths

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Intervalance 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 intervalance 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⁻ = PF₆⁻, BF₄⁻, or ClO₄⁻) is found to vary inversely with the solvent’s static dielectric constant, $D_0$. When the ion-pairing effects are eliminated by dilution, a genuine test of the Marcus–Hush prediction of the solvent dependence of the intervalance charge-transfer energy ($E_{MCT}$) is possible. For highly polar solvents ($D_0 \gtrsim 20$) a good fit of $E_{MCT}$ to $1/D_0 - 1/D_l$ is found (where $D_l$ is the optical dielectric constant and $1/D_0$ is the main variant in the two-term dielectric parameter). For methylene chloride, however, $E_{MCT}$ 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 CD₂CN, $E_{MCT}$ 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 intervalance 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. Bond reorganization effects, the Marcus "inverted region", and distance-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. 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 intercalation methods. Recently, however, the fundamental validity of the solvent reorganization concept, at least for intramolecular ET reactions, has been called into question (see eq 1). 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. As suggested by the Marcus-Hush expression

\[ \chi_s = e^2(1/r - 1/d)(1/D_{op} - 1/D) \]  

(1)

this leads to a number of simple predictions about the way in which the solvent reorganization energy (\( \chi_s \)) should depend upon reactant and medium properties. In eq 1, \( r \) 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 \( D \) the static dielectric constant of solvent.

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

\[ \chi_s = \chi_1 + \chi_2 + \Delta E + \Delta E' \]  

(3)

doing so, one can make similar points.

The catalyst that eventually led to the direct evaluation

\[ E_{op}^{\text{MMCT}} = \chi_2 + \chi_3 + \Delta E + \Delta E' \]  

(3)
of eqs 1 and 3 by optical intercalation measurements was the synthesis in 1969 of solution-based dinuclear mixed-valence complexes. The solvent dependence (\( E_{op}^{\text{MMCT}} \propto (1/D_{op} - 1/D) \)) was verified by Tom et al. in 1974,40 the distance dependence by Powers and Meyer in 1976,41 the dependence on \( \Delta E \) by Goldsby and Meyer in 1984,12 and the dependence on \( \Delta E' \) by Kober et al. in 1983.33 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 \( E_{op}^{\text{MMCT}} \), and especially \( \chi_2 \), 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 intercalation 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 \( E_{op}^{\text{MMCT}} \) 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, \( E_{op}^{\text{MMCT}} \) has been found in several instances to depend on both the mixed-valence chromophore concentration and the concentration of added electrolyte.6b,16 Neither result is expected superficially from eq 1. Second, when \( D_{op} \) (but not \( D_{op} \)) is decreased drastically (ca. 10-fold) by pressure-induced freezing, \( E_{op}^{\text{MMCT}} \) fails to respond or at best decreases by only a small amount.17 Again, this is contrary to the simplest interpretation of eq 1. Furthermore, as Hammack and co-workers have pointed out,5b 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 \( D_{op} \) has not been satisfactorily examined. Third, in at least two cases involving strong ligand–solvent hydrogen bonding (HB), \( \chi_2 \) has been shown to vary with solvent HB parameters rather than with dielectric parameters.6e,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 \( E_{op}^{\text{MMCT}} \) increases with increasing ionic strength—has been linked by most investigators to ion pair (or ion aggregate) formation.16,18 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 intercalation transfer energy most probably comes from induced displacement of initial- and final-state zero-point energies,16 a conclusion reached also by Lowery et al.58 This displacement, of course, is just the \( \Delta E \) 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 \( \Delta E \) term is in the ion-pairing-induced structural inequivalence of the MMCT reactant and initially formed photoprodut, e.g.

\[ \text{Fc}^-\text{C}==\text{C}^-\text{Fc}^+ \xrightarrow{\text{hv}} \text{Fc}^-\text{C}==\text{C}^-\text{FcX}^*- \]  

(4)

where \( \text{Fc} \) 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 \( X = \text{PF}_6^- \) and methylene chloride as solvent, we have previously shown16 that correction of \( E_{op}^{\text{MMCT}} \) 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 \( \Delta E \) and \( \Delta E' \) equal to zero) did not lead to particularly close agreement. Furthermore, as various workers have pointed out,15,36 the ion-pairing-induced variations in \( E_{op}^{\text{MMCT}} \) 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.

(18) As we shall see, as a practical matter "infinite dilution" can often be reasonably approximated by the millimolar concentrations typically employed in intercalation charge-transfer experiments.
(19) Hammack and co-workers5b along with Lewis and Obeng6a have made similar points.
TABLE I: Solvent Dependent Intervalence Energies and Bandwidths for Acetylene-Bridged Biferrocene at Infinite Dilution

<table>
<thead>
<tr>
<th>solvent</th>
<th>( D_{op} )</th>
<th>( D_{sp} )</th>
<th>( 1/D_{op} - 1/D_{sp} )</th>
<th>( E_{op}^{MMCT} ), cm(^{-1} )</th>
<th>( \Delta \eta_{ij}^{(exp)} ), cm(^{-1} )</th>
<th>( \Delta \eta_{ij}^{(calc)} ), cm(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetonitrile-d(_3)</td>
<td>1.807</td>
<td>37.5</td>
<td>0.526</td>
<td>7350</td>
<td>4000(^d)</td>
<td>4120</td>
</tr>
<tr>
<td>acetone-d(_4)</td>
<td>1.841</td>
<td>20.7</td>
<td>0.496</td>
<td>7350</td>
<td>4100(^d)</td>
<td>4120</td>
</tr>
<tr>
<td>nitromethane-d(_4)</td>
<td>1.909</td>
<td>38.6</td>
<td>0.498</td>
<td>7000</td>
<td>4100(^a)</td>
<td>4020</td>
</tr>
<tr>
<td>benzonitrile</td>
<td>2.338</td>
<td>25.2</td>
<td>0.388</td>
<td>6340</td>
<td>4150(^b)</td>
<td>3820</td>
</tr>
<tr>
<td>nitrobenzene-d(_4) chloride</td>
<td>2.403</td>
<td>34.8</td>
<td>0.384</td>
<td>6250</td>
<td>4250(^b)</td>
<td>3800</td>
</tr>
<tr>
<td>acetonitrile-d(_4)</td>
<td>(1.81)(^f)</td>
<td>43.3(^g)</td>
<td>(0.529)(^g)</td>
<td>(~750)(^a)</td>
<td>(~3300)(^d)</td>
<td></td>
</tr>
<tr>
<td>acetonitrile-d(_4)</td>
<td>(2.1)(^g)</td>
<td>3.9(^g)</td>
<td>(0.22)(^g)</td>
<td>(~565)(^a)</td>
<td>(~2450)(^d)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)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. \(^d\)Fall at half-width. \(^e\)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 5c. \(^h\) Taken from ref 5c. \(^i\)For 2.3 mM BF\(_4\)\(^\text{-}\), taken from Figure 1 of ref 5c. \(^j\)\( P = 1 \text{ kbar; liquid.} \(^k\)\( P = 5.5 \text{ kbar; solid.} \)

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 quantify the ion-pairing relation (eq 5) which links eqs 2 and 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.\(^l\)\(^m\) Our target system in all experiments was the acetylene-bridged biferrocene monocation (BF\(^+\)). The choice was motivated by (1) the existence from our own lab\(^n\) and elsewhere\(^o\) 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\(^p\) 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.\(^q\) 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.\(^2\)) The mixed-valence compound was obtained as a solid hexafluorophosphate salt by oxidation in toluene (99+%), (HPLC grade) were all purchased from Aldrich. The first seven were used as received. The last three were used after passage 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 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\(_6^\text{-}\)) in several solvents: (A) full scale, (B) expanded concentration scale. Key to solvents and electrolytes (from top): (0) acetonitrile-d\(_3\) + TBA \(_4\)BF\(_4\); (\( \bullet \)) acetone-d\(_4\) + TBA \(_4\)PF\(_6\); (\( \circ \)) nitrobenzene-d\(_4\) + TBA \(_4\)BF\(_4\); (\( \bigcirc \)) nitrobenzene-d\(_4\) + TBA \(_4\)PF\(_6\); (\( \bigcirc \)) methylene-d\(_3\) chloride + TBA \(_4\)PF\(_6\).

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Figure 2. $E_{\text{MMCT}}^{\text{EMC}}$ versus $(1/D_{\text{op}} - 1/D_{s})$ for open circles, $Bf^+PF_6^-$ at unspecified (ca. millimolar) concentrations (ref 20); triangles, 2.3 mM $Bf^I$ (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 ($T = 25{}^\circ\text{C}$, $P = 5.5$ kbar).

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

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Electrolyte</th>
<th>$K_{IP}$ M$^{-1}$</th>
<th>$K_{IP}E_{\text{EMC}}^{\text{EMC}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{acetone-d}_5$</td>
<td>NaClO$_4$</td>
<td>66</td>
<td>8</td>
</tr>
<tr>
<td>$\text{acetone-d}_6$</td>
<td>TBA$^+Bf^-$</td>
<td>40</td>
<td>9</td>
</tr>
<tr>
<td>$\text{acetonitrile-d}_4$</td>
<td>TBA$^+Bf^-$</td>
<td>180</td>
<td>6</td>
</tr>
<tr>
<td>$\text{acetonitrile-d}_5$</td>
<td>$\text{TBA}^+\text{PF}_6^-$</td>
<td>370</td>
<td>38</td>
</tr>
<tr>
<td>$\text{nitromethane-d}_4$</td>
<td>$\text{TBA}^+\text{PF}_6^-$</td>
<td>70</td>
<td>5</td>
</tr>
<tr>
<td>$\text{dichloromethane-d}_4$</td>
<td>$\text{TBA}^+\text{PF}_6^-$</td>
<td>9000</td>
<td>31</td>
</tr>
</tbody>
</table>

*Activity corrections and electrolyte self-association effects neglected.

The dilute-solution absorption spectra in pyridine-$d_4$, tetramethylethylene, 1-methyl-2-pyrrolidinone, dimethyl-$d_4$ sulfoxide, and propylene carbonate. (We were able to obtain spectra in 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 $E_{\text{MMCT}}^{\text{EMC}}$ 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 $E_{\text{MMCT}}^{\text{EMC}}$ values versus the dielectric parameter $(1/D_{\text{op}} - 1/D_{s})$. Included for comparison are data collected by Powers and Meyer at roughly millimolar concentrations.

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). 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 $[\Delta E_{\text{MMCT}}^{\text{EMC}}(100\%)/E_{\text{MMCT}}^{\text{EMC}} - E_{\text{MMCT}}^{\text{EMC}}(\text{initial})] - 1$ versus $1/\gamma[X]$ (see Table II). In the plot, $\Delta E_{\text{MMCT}}^{\text{EMC}}(100\%)$ represents the difference in interconversion transition energy between the completely paired and completely unpaired complexes, while $\gamma$ is the mean ionic activity coefficient for the added electrolyte. (Values were obtained from the extended Debye-Hückel equation with appropriate corrections for electrolyte self-association.) Linear plots were obtained in most cases the reason for failure appeared to be either solv délusion or further chemical degradation of the mixed-valence ion. 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. We previously reported the second equilibrium to ion tripling, and indeed this may be correct when the counterion source is chiefly the added electrolyte (TBA$^+\text{PF}_6^-$). When the chromophore and its counterion are exclusively present, however, ion tripling is possible only at the expense of ion pairing:

$$\text{Br}^+\text{PF}_6^- + \text{Br}^+\text{PF}_6^- = \text{Br}^+ + \text{Br}^+\text{PF}_6^-$$

(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., $\text{Br}^+\text{PF}_6^- = (\text{Br}^+\text{PF}_6^-)_2$, where the overall aggregation could presumably occur by a succession of $n$ individual steps).

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

$$\Delta\nu_{1/2} = [16(\ln 2)kT(\chi_1 + \chi_2)]^{1/2} = [16(\ln 2)kT(E_{\text{op}}^{\text{EMC}} - \Delta E - \Delta E)]^{1/2}$$

Table II lists values for $\Delta\nu_{1/2}$ calculated from the right-hand side of eq 7. In the calculation, $\Delta E$ was assumed to be negligible and $\Delta E$ was forced to zero by choosing $E_{\text{op}}^{\text{EMC}}$ 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., $\text{Br}^+\text{PF}_6^-$), 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. In replicating those findings in the present study, the most notable observation was the systematic broadening and then narrowing of the interconversion band as the extent of ion pairing increased. Also significant is the observation that the maximum widths occurred near 50% ion pairing, this provides an independent proof for the existence of two MMCT chromophoric species.

(27) See, for example: Borchardt, D.; Wherland, S. Inorg. Chem. 1984, 23, 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$_2$Cl$_2$ differs slightly from that reported in ref 16, even though the same experimental data were employed. The difference comes from a revised value for $E_{\text{op}}^{\text{EMC}}(\text{initial})$ and therefore, $\Delta E_{\text{op}}^{\text{EMC}}(100\%)$. The revised value for the former is 4760 cm$^{-1}$. We previously relied upon a curved extrapolation to estimate $E_{\text{op}}^{\text{EMC}}(\text{initial})$. The evaluation can be linearized, however, by constructing a plot of $(\Delta E_{\text{op}}^{\text{EMC}}(100\%)/E_{\text{op}}^{\text{EMC}} - E_{\text{op}}^{\text{EMC}}(\text{initial}) - 1)$ versus $[X]$ and imposing the condition (by adjusting $\Delta E_{\text{op}}^{\text{EMC}}(100\%)$ for the intercept equal zero.)


(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.
validation of the above estimates of $K_{IP}$.

Discussion

Perhaps the most surprising finding in view of the previous work on both $\text{Bi}^+$ in dichloromethane and biferrocene monocation in nitrobenzene is just how little the new $E_{\text{MCT}}$ values\(^{(28)}\) 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 $[X^-] \leq 1 \text{ mM}$. 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 in $K_{IP}$ and $1/D_i$. 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–Hash theory really work? Figure 2 demonstrates very clearly that when ion-pairing artifacts are absent, the energy for intervalence transfer in $\text{Bi}^+$ displays the expected dependence on $1/D_{\text{op}}$. (Note, however, that apart from CD$_2$Cl$_2$, frozen acetonitrile, and perhaps acetone as solvent, variations in the magnitudes of ion-pairing constants. Figure 3 shows that a useful (and potentially predictive) correlation does exist between in $K_{IP}$ and $1/D_i$. The correlation is expected, of course, if the differences in ionic association are due mainly to differences in Coulombic attraction.

Returning to the question of the dependence of $E_{\text{MCT}}$ on the static dielectric constant, Figure 2 suggests a mixed result. When $D_i$ 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)\(^{(29)}\) to $1/D_{\text{op}} = 1/D_i$ (however, see later discussion). On the other hand, when $D_i$ is substantially decreased by simply changing the identity of the liquid solvent (to CD$_2$Cl$_2$, frozen acetonitrile, and perhaps acetone as solvent, variations in the $D_i$ term are negligible). Admittedly, the plot shows nearly a 2-fold smaller slope than predicted by eq 1 (based on $r = 3.9 \text{ Å}$ and $d = 7.3 \text{ Å}$ (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.\(^{(14,17)}\) Since we have nothing new to contribute to this particular discussion, we will not reiterate the explanations.

Returning to the question of the dependence of $E_{\text{MCT}}$ on the static dielectric constant, Figure 2 suggests a mixed result. When $D_i$ 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)\(^{(29)}\) to $1/D_{\text{op}} = 1/D_i$ (however, see later discussion). On the other hand, when $D_i$ is substantially decreased by simply changing the identity of the liquid solvent (to CD$_2$Cl$_2$, there is an unexpectedly large decrease in energy. In other words, $D_i$ behaves as if it were even smaller (and $1/D_i$ 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 $\text{Bi}^+$, the solvent dielectric response is field saturated and the local dielectric strength is less than $D_i$.\(^{(31)}\) At a microscopic level, the saturated effect might be attributed to a loss of vibrational or electronic 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, $D_i$ decreases, $\chi$ is predicted to decrease, and consequently $E_{\text{MCT}}$ should decrease if there are no other energy effects.\(^{(32)}\) Although the existing data (Figure 2) seem to confirm the predictions (at least approximately), we regard the agreement as fortuitous. Recall that the frozen solvents were performed with 2.3 mM $\text{Bi}^+$;\(^{(56)}\) At this concentration, the chromophore and its counterion would almost certainly be completely associated and a substantial blue shift in $E_{\text{MCT}}$ would be expected. If ion pairing were the only form of association, the magnitude of the shift would be $\Delta E_{\text{MCT}} = -RT \ln K_{IP}/K_{IP}$, 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. $5 \times 10^7 \text{ M}^{-1}$. 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 $\Delta E_{\text{MCT}}$ also increases approximately with $\ln K_{IP}$. Extrapolating from the liquid solvents, $\Delta E_{\text{MCT}}$ is estimated to be ca. 1900 cm$^{-1}$ in frozen acetonitrile. Neglecting other factors, this would place the point for frozen CD$_2$CN 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 $E_{\text{MCT}}$. 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 $E_{\text{MCT}}$ chiefly through $\Delta \varepsilon$ (eq 3)\(^{(28)}\) but that dielectric saturation should exert an influence on $\chi$, through $\chi$. One means of separating the effects would be to evaluate intervalence bandwidths, since these are expected to respond only to $\chi$ (provided that only one chromophore is present; see Results section). Table I shows that there is a substantial decrease in $\Delta \varepsilon_{1/2}$ (and by inference, $\chi$) upon freezing the solvent. If the bandwidth is then employed to calculate just the reorganization part of $E_{\text{MCT}}$ (eq 6), the value is ca. 2600 cm$^{-1}$. This can be compared with the overall (measured) value of 5650 cm$^{-1}$ (Table 1). On this basis, an energy deficit of about 3000 cm$^{-1}$ exists. Recall, however, that the quantity $-RT \ln K_{IP}/K_{IP}$ could 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 ion-pair aggregation. This could be an oversimplification of the charging mechanism, as multiple higher order ionic association processes may be present. Second, in our treatment of the mixed-valence species, we have used $K_{IP}$ as a measure of the stability of the complex. This is a reasonable approximation if the complex is essentially complete and a substantial blue shift in $E_{\text{MCT}}$ would occur. The complexity of the mixed-valence species is that apart from CD$_2$Cl$_2$, frozen acetonitrile, and perhaps acetone as solvent, variations in the magnitudes of ion-pairing constants. Figure 3 shows that a useful (and potentially predictive) correlation does exist between in $K_{IP}$ and $1/D_i$. The correlation is expected, of course, if the differences in ionic association are due mainly to differences in Coulombic attraction.

(29) Actually, in methylene chloride or acetone as solvent the maximum bandwidths 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, $E_{\text{MCT}}$ (final) might be underestimated. In the acetonitrile case, arbitrary adjustment of $E_{\text{MCT}}$ (final) to cause $\Delta \varepsilon_{1/2}$ to maximize at 50% ion pairing, leads to a value of $310 \text{ M}^{-1}$ 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$_2$Cl$_2$ lies more than 30 below the best-fit line for the remaining solvents.

(31) A related explanation involving a frequency-dependent ion 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.
Molecular Structure and Conformation of Dilsopropyl Ketone Studied by Gas Electron Diffraction Combined with Vibrational Spectroscopy and SCF MO Calculations

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The molecular structure and conformation of dilsopropyl ketone, Me₂C(3)HC(2)OC(4)HMe₂, 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 C₁, C₃, and C₄ symmetry exist with the molar fractions of 0.45 (31), 0.31 (12), and 0.24 (22), respectively. The dihedral angles φ(C₁C₂C₃H) and φ(C₁C₂C₄H) of the C₁, C₃, and C₄ conformers (the values are denoted by φ₁ and φ₂) are (16°, -62°), (0°, 180°), and (59°, 59°), respectively, where φ₁ and φ₂ are defined to be zero when the C-C bond eclipses the C-H bond. The main structural parameters (rₑ and θₑ) of the C₁ conformer with the limits of error (3σ) in parentheses are as follows: r(C-C) = 1.215 (5) Å, r(C-C) = 1.535 (2) Å, r(C-H) = 1.118 (3) Å, d(C=O) = 1.166 (17) Å, θ(CCC) = 110.8 (4)°, and θ(CCHMe) = 111.1 (9)°, where the symbol ( ) denotes average values.

Introduction

The conformational studies of dilsopropyl ketone (DIK) have been investigated by several authors with different conclusions. Aroney and co-workers measured the molar Kerr constant of DIK in CCl₄ solution. They assumed the presence of two conformers, one in which both H₁,₂,₃,₄ atoms are anti to the oxygen atom (C₄ symmetry) and the other in which one H₁,₂,₃,₄ atom is syn to the oxygen atom and the other is anti to the oxygen atom (C₃ symmetry). Here, H₁,₂,₃,₄ 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 measured the infrared spectra of DIK and related ketones in CCl₄ solution and concluded from the carbonyl stretching frequencies that the two H₁,₂,₃,₄ atoms of the predominant conformer of DIK are eclipsed with the oxygen atom (C₄ symmetry). Suter 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 C₃ symmetry with the dihedral angle, φ₁(C₁C₂C₃H) = φ₂.