Solvent Effects on Electronic Coupling between Dialkylamino Groups in Aromatic Diamine Radical Cations

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Solvent Effects on Electronic Coupling between Dialkylamino Groups in Aromatic Diamine Radical Cations

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The transition energies (E_{op}) for the intervalence bands of the radical cations from N,N,N',N'-tetramethyl-*p*-phenylenediamine, 1,4-bis(9′-azabicyclo[3.3.1]non-3′-one-9-yl)benzene, and N,N,N',N'-tetramethyl-4,4′-di-aminobiphenyl have been determined in eleven solvents varying in polarity from chloroform to acetonitrile. Assuming the Marcus−Hush two state model $E_{op} = 2H_{op}$, where H_{op} is the matrix coupling element between the charge-bearing dialkylamino units of these delocalized systems. H_{op} is detectably sensitive to solvent, varying 140, 70, and 110 cm^{-1}, respectively. A trend for dependence of H_{op} on the refractive index of the solvent (n) is observed, H_{op} increasing slightly as $n^{-1/2}$ increases. Empirical fit to the observed H_{op} values suggests that in addition to the n effect, there is quite compound-specific sensitivity to solvent donor number. Sensitivity of H to solvent is of similar magnitude for the localized bis(hydrazine) intervalence cation 22H$^+$, using Hush's method for evaluating H from the charge-transfer band parameters (we call this number H_H). The H_H values show the opposite solvent refractive index effect, H_{op} decreasing as $n^{-1/2}$ increases. However, when the extinction coefficient (ϵ_{max}) correction suggested by the Kodak group is introduced into the Hush equation, a slight increase in H with $n^{-1/2}$ that is qualitatively similar to that found for the delocalized systems is obtained. This suggests to us that a refractive index correction to ϵ_{max} should be used.

Introduction

Electron transfer (ET) reactions are of fundamental importance in chemistry and biology, and a great deal of effort has been put into understanding them. ET theory was initially developed by Marcus,[1] who emphasized the importance of the total vertical reorganization energy λ and the electronic coupling matrix element that measures the electronic interaction between the charge-bearing units (H) in determining the ET rate constant. λ may be broken into additive components, the solvent reorganizational energy λ_s, and the internal vibrational reorganization energy λ_v because the frequencies associated with solvent and internal geometry reorganization are very different. The total vertical reorganizational energy λ quite obviously decreases as the solvent becomes less polar. By assuming that the solvent may be considered a dielectric continuum, Marcus introduced a very simple equation that makes λ_s directly proportional to the Pekar factor γ. The Pekar factor depends only upon bulk solvent parameters, the refractive index at the sodium D line (n) and the static dielectric constant, ϵ_s: $\gamma = 1/n^2 - 1/\epsilon_s$. This paper focuses on whether H also depends detectably upon solvent. Zimmt and co-workers have especially studied molecules having special geometric features causing a large solvent effect on H.[2] They prepared $^+$D−C−A$^-$ molecules in which charge separation between D and A has been photoinduced, and the bridge C has the shape of a C-clamp, making D$^+$ and A$^-$ lie rather close, but allowing solvent molecules between them. There is a very small H for through-bond ET because the pathway through C is long. Charge return rate constants are

significantly affected by solvent because a much shorter distance, through-solvent pathway for ET is available. This paper will focus on how important solvent is in determining H in the absence of such effects.

The most revealing ET systems ever devised are symmetrical, localized, intervalence (IV) compounds, called Robin-Day class II systems.[3] They may be symbolized as M−B−M$^+$ because they have identical charge-bearing units (M) symmetrically attached to a bridge (B), but they are at an oxidation state that places different charges on M. The bridge controls the relative orientation of the units, determining the average ET distance (d) and making it likely that a single ET transition state is involved, while the identical M units fix $\Delta G°$ for ET at zero. Class II IV compounds show a charge transfer (CT) absorption band corresponding to excitation from the ground state with charge localized on one M unit to the excited state, with charge localized on the other M. We will call this band the Hush-IV band, to distinguish it from other IV−CT bands. Hush pointed out that when the parabolic diabatic energy surfaces (those in the hypothetical absence of H) used by Marcus are assumed, the transition energy of the Hush-IV band (E_{op}, the photon energy ν at the band maximum) is equal to Marcus' λ, and introduced determination of H from experimental parameters of the Hush-IV band and the electron-transfer distance d.[4]

When H exceeds $\lambda/2$ for a symmetrical IV compound, the system becomes charge-delocalized (Robin-Day class III).[3] The Hush-IV absorption band for a class III compound involves some charge redistribution, but not the charge transfer between

**TABLE 1: Bulk Solvent Parameters and H_{Op} Values for Class III IV Compounds at Room Temperature**

solvent	bulk properties			$TMPD^+BF_4^-$		$k33)_2PD^+PF_6^-$		$TMB^+BF_4^-$	
	γ	$n^{-1/2}$	DN	λ_{max} (nm)[a]	H_{op} (cm^{-1})	λ_{max} (nm)[a]	H_{op} (cm^{-1})	λ_{max} (nm)[a]	H_{op} (cm^{-1})
DMSO	0.437	0.823	29.8	624	8013	622	8037	1040	4807
DMF	0.463	0.837	26.6	620	8065	620	8065	1030	4854
acetone	0.495	0.859	17.0	615	8130	617	8104	1019	4907
PrCN	0.482	0.850	16.6	614	8143	618	8091	1021	4897
EtCN	0.501	0.856	16.1	614	8143	617	8104	1020	4902
MeCN	0.528	0.864	14.1	614	8143	617	8104	1019	4907
PhCN	0.390	0.810	11.9	621	8152	623	8026	1039	4859
tetrahydrofuran	0.375	0.842	20.0	617	8104	619	8078	1026	4873
CH2Cl2	0.383	0.839	[0]	616	8117	623	8026	1029	4859
CHCl3	0.268	0.832	[0]	615	8130	617	8104	1025	4878
ethyl formate	0.401	0.858		614	8143	617	8104	1017	4916

[a] Values reported are the maximum of the 0,0 band, also the highest absorbance for the IV band.

the charge-bearing units that is involved for class II compounds. We believe that Creutz first pointed out explicitly that E_{op} no longer measures λ, but is equal to $2H$ in the Marcus−Hush two state model.[5] We will designate H values obtained from E_{op} for class III compounds as H_{op}, to distinguish them from H values obtained by other means. The $H_{op} = E_{op}/2$ relationship involves no assumption about diabatic surface shape or the quantum-mechanical description of the Hush-IV band. It does assume that a two state description having no direct overlap between the charge bearing units is adequate[6] and that the transition is vertical.[7] The determination of through bond orbital, orbital interactions was pioneered by Hoffmann and by Gleiter, and Paddon-Row especially studied the photoelectron spectroscopic splitting between the π orbital combination bands for symmetrical polycyclic bis-alkenes.[8] Hush explicitly noted that the $H = E_{op}/2$ relationship allows easy extraction of H values from such data, because H is half the π-dominated orbital splitting (for systems that give class III radical cations having negligible geometry change between the neutral and radical cation oxidation states, and when direct overlap between the π systems is not present).[4a,9] This work concerns the experimental determination of the solvent effect on H, using the expression $E_{op} = 2H_{op}$, for three symmetrical, class III aromatic-bridged diamine radical cations, and comparison with data for a class II system.

Results: Dependence of H_{op} on Solvent for Class III Intervalence Compounds

H_{op} can obviously be determined more accurately for a class III compound than it can be estimated from the IV band of any class II compound (see below). We have determined the solvent dependence of H_{op} for some organic-centered class III compounds here. H_{op} cannot be measured accurately for metal-centered systems, where the relatively small metal, bridge coupling typically places E_{op} in the IR region, and the great width and low extinction coefficient make the Hush-IV band hard to even detect. In contrast, the untwisted, R_2N-centered charge-bearing units of the compounds studied here place E_{op} in the visible or near-IR, where it may be measured easily.[10] Tetramethyl-p-phenylenediamine radical cation ($TMPD^+$) and its bis-γ-keto-substituted bicyclic diamine analogue ($k33)_2PD^+$) share the same eight atom π system (a five bond pathway between the nitrogens) and have almost the same E_{op} value in acetonitrile (MeCN). Tetramethylbenzidine radical cation (TMB^+) has a nine bond pathway between the nitrogens, resulting in only 60% as large an H_{op}. As discussed in detail recently,[10] all three are class III intervalence compounds having negligible overlap between their R_2N charge-bearing units. Density functional theory calculations by Brouwer that agree with

TMPD   **k33)₂PD**

TMB   **22H**
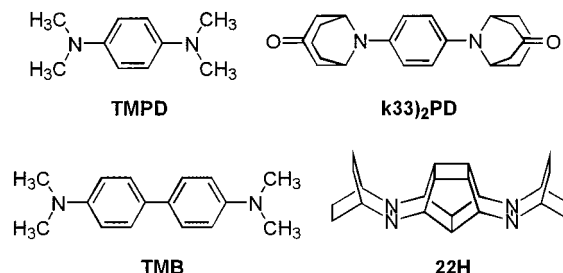
previously published Raman spectra for $TMPD^+$ demonstrate independently that it is delocalized.[11] The class III compounds of Table 1, like both class II and class III metal-centered systems, have a distance dependence of H_{op} that is consistent with expectation, when the $H_{op} = E_{op}/2$ relationship is employed for the class III systems. All three compounds have nearly vertical *IV* transitions that show vibrational structure with the 0,0 band as the strongest vibrational component, so E_{op} (and hence H_{op}) can be measured accurately. We estimate the uncertainty in locating the 0,0 band absorption maximum of the Hush-IV band λ_{max} for these compounds at ±1 nm, corresponding to H_{op} uncertainty of ± 13 cm^{-1} for the PD$^+$ derivatives and 5 cm^{-1} for TMB$^+$. The λ_{max} and resulting H_{op} values in 11 solvents are given in Table 1. Although E_{op} varies detectably for the compounds of Table 1, these class III systems show far less sensitivity to solvent than any class II system, where $E_{op} = \lambda$, and λ_s depends significantly on solvent.

Discussion: Class III Compounds

The insensitivity of class III compound IV−CT bands to solvent changes has always been used as a diagnostic character for them being in class III,[4,5] although it should be noted that the bands examined have not been the Hush-IV band.[12] Kim and Hynes discussed solvent effects predicted by dielectric continuum theory on line shapes for class III compounds,[13] but we have not seen discussion of the solvent effects expected upon E_{op}, presumably because they are so small. We do not expect that Hush-IV absorptions for class III compounds are fundamentally different from electronic transitions in other types of molecules, and finding small solvent effects on transition energies is common. Nevertheless, E_{op} for the Hush-IV band of class III compounds has the special interpretation of being $2H$ in the two state model. The total ranges of H_{op} observed are 140 cm^{-1} (1.7%) for TMPD$^+$, 70 cm^{-1} (0.8%) for k33)$_2$PD$^+$, and 110 cm^{-1} (2.3%) for TMB$^+$. H_{op} for these class III compounds is about as sensitive to solvent as is H_H of the class II **22H**$^+$ (see below), although the percentage change is smaller for the class III compounds because H_{op} is larger. Theoreticians have often expected solvent effects on optical absorptions to
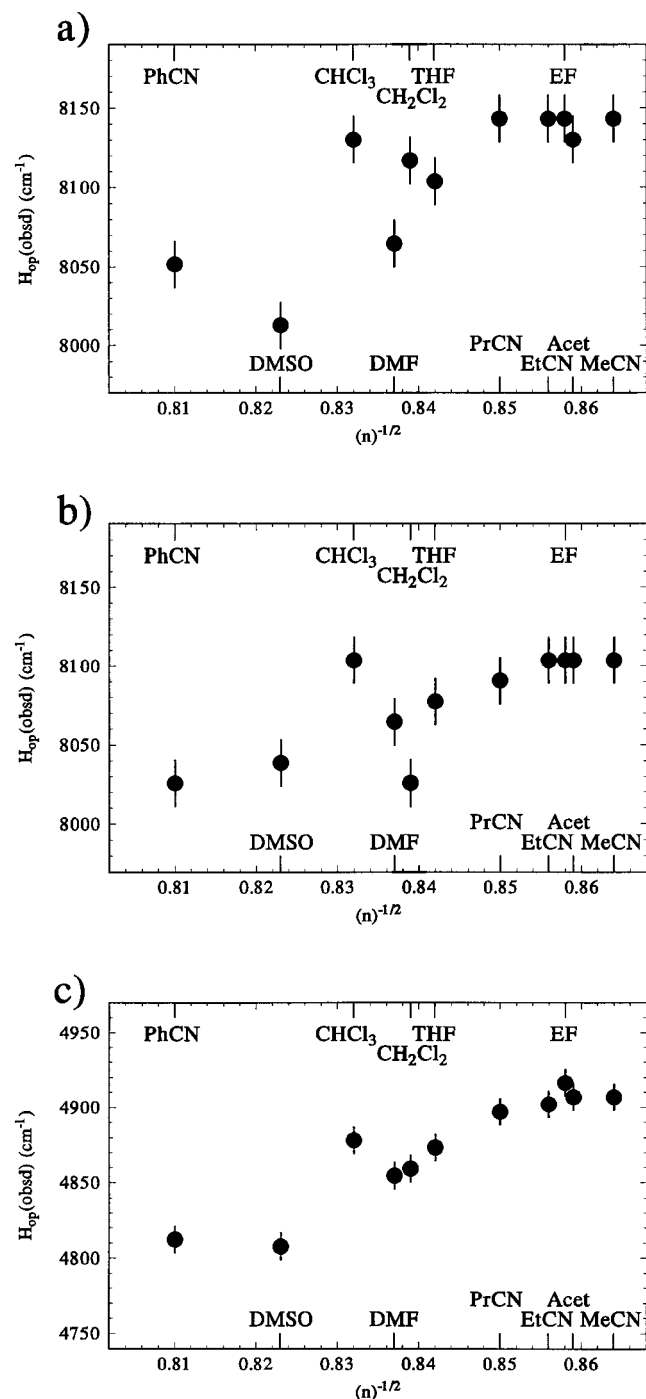
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Figure 1. Plots of H_{op} for Class III compounds as a function of $(n)^{-1/2}$. (a) TMPD$^+$. (b) k33)$_2$PD$^+$. (c) TMB$^+$.

Figure 2. Plots of H_{op}(obsd) versus H_{op}(calcd) using eq 3 and the constants from Table 2 for (a) TMPD$^+$ (open circles), 33)$_2$PD$^+$ (diamonds). (b) TMB$^+$.

TABLE 2: Empirical Fitting Parameters for H_{op}(calcd) $= A + B(DN) + C(n)^{-1/2}$

compound	TMPD$^+$	33)$_2$PD$^+$	TMB$^+$
A	6202	6093	3035
B	−2.2	+1.5	−0.5
C	2300	2320	2190

correlate with bulk solvent properties, and we examined the H_{op} values observed for such trends. As shown in Figure 1, for the more polar solvents studied, there is a roughly linear correlation of H_{op} with $n^{-1/2}$ (or with n^{-2} or γ—over the small range of n available; the n^{-2} term of γ greatly predominates for high ϵ_s solvents).[14] There is a slight increase in H_{op} as $n^{-1/2}$ increases for these class III compounds.

We also examined what else besides n affects the H_{op} values (see Table 1 for bulk solvent parameters). Solvent donicity, as measured by Gutmann's solvent donicity numbers (DN),[15] appears to influence H_{op} enough that we have not been able to obtain good correlations without using it. Solvent donicity is a nondielectric continuum effect that clearly tends to raise E_{op} for class II nitrogen-centered *IV* compounds.[16] The simplest
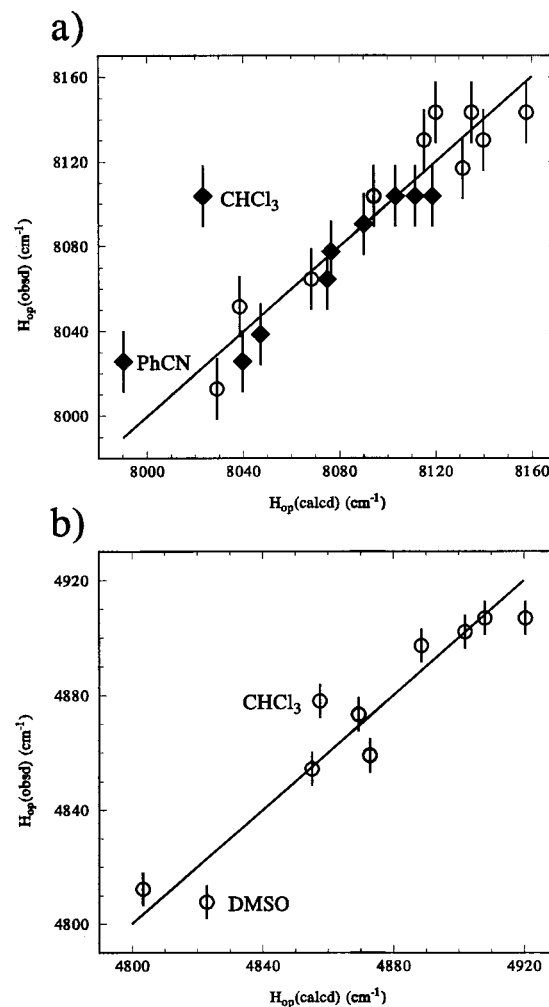
expression that successfully correlates the H_{op} values for these class III compounds includes terms for both $(n)^{-1/2}$ and DN, see eq 1. The constants for best fit to eq 1 appear in Table 2, and plots of H_{op}(obsd) versus

$$H_{op}(\text{calcd}) = A + B(\text{DN}) + C(n)^{-1/2} \qquad (1)$$

H_{op}(calcd) are shown as Figure 2. The average deviation of H_{op}(calcd) from the experimental numbers is 12.8 cm^{-1} for TMPD$^+$ in all 10 solvents available (we have not located a DN value for ethyl formate) and excluding the least polar solvent, chloroform (deviation, 80 cm^{-1}), is 10.3 cm^{-1} for k33)$_2$PD$^+$ and 6.6 cm^{-1} (chloroform deviation 21 cm^{-1}) for TMB$^+$. These average deviations are comparable to the 13, 13 and 5 cm^{-1} error we estimate in obtaining H_{op}(obsd), so the fit to eq 1 is rather good.[17,18] As for E_{op} of class II nitrogen-centered *IV* compounds,[16] the dependence on *DN* is very sensitive to both the alkyl groups present and the bridge. Although TMPD$^+$ and 33)$_2$PD$^+$ have the same π system, their *B* coefficients are very different, even in sign. We presume that this occurs because

solvent donicity involves specific (nondielectric continuum) interactions between the solvent and the cation. Ion pairing certainly occurs in low ϵ_S solvents such as CH_2Cl_2.[19] Class III compounds that are ion paired or strongly interacting with donor solvents might be unsymmetrical, although nothing is known about their structures, and it is not obvious how such interactions would affect H. Because both ion paired and non-ion paired systems are fit by eq 1, such affects are apparently rather small.

Discussion: Solvent Effects on H for Class II Intervalence Compounds

Hush's familiar equation for obtaining H for class II compounds (which we will designate H_H to distinguish from other methods) is eq 2,[4] where $\Delta\tilde{\nu}_{1/2}$ is the bandwidth at half-height,

$$H_H = 0.0206(E_{op}\epsilon_{max}\,\Delta\tilde{\nu}_{1/2})^{1/2}/d \qquad (2)$$

ϵ_{max} is the extinction coefficient at the band maximum, and d is the ET distance.[4] As Hush pointed out, what is needed to evaluate H is the transition dipole, and eq 2 represents a simple approximation to obtain it for idealized band shape. The optical spectra of many examples of class II compounds with transition metal-centered M have been analyzed using simple Hush theory, as well as other methods.[5] We have prepared several dinitrogen-centered systems that undergo adiabatic electron transfer for which both the thermal rate constant for electron transfer and the optical spectrum can be measured and found that H values from eq 2 lead to rate constants that are as accurate as uncertainties in d and possible modifications to eq 2 (see below) allow.[20] Elliott and co-workers have recently compared rate constants for thermal and optical ET in a ruthenium-centered system that undergoes nonadiabatic electron transfer, also finding rather good agreement with H calculated using eq 2.[21]

Although eq 2 does not include explicit solvent effects, E_{op}, ϵ_{max}, and $\Delta\tilde{\nu}_{1/2}$ are all detectably solvent dependent. The ET distance d has been assumed not to be solvent sensitive, and d cannot be directly measured to test whether it is. The most studied IV compounds are ruthenium(II,III)-centered systems,[5] and rather large effects of solvent on H have been suggested for some. For example, Crutchley and co-workers report 22%–31% smaller H values (estimated from thermodynamic measurements, using constant d values for all compounds) in dimethylsulfoxide (DMSO) than in acetonitrile (MeCN) for eight diruthenium dicyanamido-benzene IV complexes.[22] Our group has studied several bis(hydrazine) and bis(hydrazyl) IV compounds that have sterically encumbered two atom π systems bearing 0 and +1 charges, so specific interaction with the solvent seems less likely. Use of eq 2 for these compounds gives H_H values that are nearly constant as solvent is changed.[23,24]

The Kodak group has introduced explicit dependence upon the refractive index of the solvent (n) into evaluating H from IV–CT bands.[25] In a rederivation of the expression for H in the context of a vibronic coupling theory (VCT) treatment,[26] Young included an electromagnetic correction to the experimental ϵ_{max} that Hush did not use. Qualitatively, the compound being observed is assumed to cause a cavity in the solvent having $n = 1$, which will result in different experimental ϵ_{max} values for different solvents in the absence of any other effect. Although the expression for calculating H using VCT looks very different from eq 2 because the reciprocal of a complex Franck–Condon sum replaces $\Delta\tilde{\nu}_{1/2}$, when applied to experimental
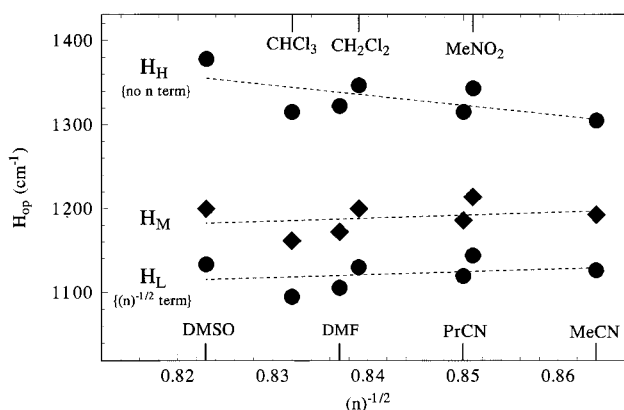

Figure 3. Plots of H_{op} for the Class II compound **22H$^+$** in various solvents as a function of $(n)^{-1/2}$ using the Hush equation (eq 2) (H_H) and including n corrections to the observed ϵ_{max}, H_L using eq 3a, and H_M using eq 3b.

spectra of dinitrogen-centered IV compounds, the result is within a few percent of being the same as using eq 2,[24] except for the correction to ϵ_{max}. They first used[25a] a correction factor suggested by Birks[27] that produces lower H values from the same experimental data by a factor of $n^{-1/2}$ (see eq 3a), but a year later they used a correction suggested earlier by Chako[28] that replaces Birks' n^3

$$H_L = H_H(n)^{-1/2} \qquad (3a)$$

term by the expression $f(n) = n(n^2+2)^2/9$, producing an intermediate-sized H value (H_M, eq 3b).

$$H_M = H_H 3(n)^{1/2}/(n^2 + 2) \qquad (3b)$$

H_L is 14% and 16% lower than H_H in MeCN and CH_2Cl_2, respectively, while H_M is 8% and 11% smaller, respectively. Although these changes in H are rather small, they are significant for calculating ET rate constants,[25] because H is a nearly additive term in the ET barrier. Having these three equations to calculate an optically derived H value (H_{op}) poses the problem of which is best to use for experimental data. We[20,24] and Elliott and co-workers[21] have the discussed differences in rate constants obtained from optically evaluated ET parameters for adiabatic and nonadiabatic ET using the above three formulations of H obtained from optical data of class II compounds. It has been pointed out that solvent as well as the solute orbitals should be considered for ET reactions,[29] although how to handle such inclusion in interpreting experiments is not clear.

No sensitivity of H to solvent was assumed in deriving both eq 2 and 3, but they will produce different sensitivity to solvent when applied to experimental data, because of the absence of n in eq 2 and its presence in both versions of eq 3. In Figure 3 we show all three H_{op} values for the bis(hydrazine) IV compound that has been studied in the most solvents, **22H$^+$**.[23b] These values were calculated using $d = 5.03$ Å, the X-ray distance between the hydrazine units of a model compound. Obviously, if d is really smaller, H_{op} should be increased proportionately. Using the H_H expression, H_{op} decreases slightly with increasing $n^{-1/2}$, roughly increasing "polarity" (total range 73 cm^{-1}, 5.6% of the smallest value), while using the n corrected expressions, it increases somewhat less (total range 52 cm^{-1}, 4.5% of the smallest value). Although the changes in H_{op} with solvent using these expressions are too small to be significant, the 245 cm^{-1} difference in H_{op} for DMSO between H_H and H_L corresponds to about a 210 cm^{-1} difference in ΔG^*, or a factor

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of 2.8 difference in ET rate constant. Although the rate constant for ET of **22H**$^+$ has been measured quite accurately by ESR,[23b] deciding which H_{op} equation fits experiment best is still ambiguous. There is uncertainty both in the d that goes into calculating H_{op} and in the energy of the barrier-crossing frequency ($\tilde{\nu}_v$) value that goes into the preexponential term of the rate constant calculation. Similar results occur for the other σ-bridged and aromatic-bridged class II IV compounds that we have studied.[20,24] The H_{op} values are close enough to constant with solvent that we cannot be sure that the differences found are not just experimental scatter, and all three H_{op} values fit well enough with the observed ET rate constant that the uncertainty in d and $\tilde{\nu}_v$ make it unclear whether eqs 2 or 3 actually gives better fit. The slight increase in H_M and H_S for **22H**$^+$ as $n^{-1/2}$ increases is consistent with the slight increases seen in the H_{op} values for the Class III compounds studied here.

Conclusions

E_{op}, and hence H_{op}, values for Class III nitrogen-centered cations are detectably solvent sensitive, and a slight increase (with significant scatter) in H_{op} is observed as n^{-12} increases. An equation including adjustable parameters for additive effects of $n^{-1/2}$ and DN changes fits the observed H_{op} in most of the solvents studied. Dependence upon DN is a nondielectric continuum effect, and the DN coefficient obtained is very sensitive to the compound studied. H_H values as a function of solvent for the class II compound 22H$^+$ estimated using Hush's eq 2 are slightly more sensitive to solvent and show the opposite trend in a plot versus $(n)^{-1/2}$ as do the H_M and H_L values, which are estimated including different adjustments for a refractive index effect on the measured ϵ_{max} (3). Uncertainties in d and $\tilde{\nu}_v$ make an experimental choice between these three equations ambiguous, but the increase in H_M and H_L as $n^{-1/2}$ increases more closely resembles the result for Class III compounds. This suggests to us that a refractive index correction to ϵ_{max} should be used in calculating H from optical data for class II compounds, independent of the theoretical arguments for doing so.[25,27,28]

Experimental Section

Commercial TMPD was oxidized to the radical cation BF$_4^-$ salt using NOBF$_4$, and k33)$_2$PD$^+$ to its PF$_6^-$ salt with NOPF$_6$, as previously described.[30] TMB was prepared by the literature method.[31] It was oxidized in situ using less than one equivalent of NOBF$_4$, as in our previous work.[10] Acetonitrile, propionitrile, and butyronitrile were washed with concentrated HCl and water and dried with potassium carbonate before distillation from 3 Å molecular sieves. Acetone and DMSO were distilled from calcium sulfate, the latter under vacuum. Chloroform, methylene chloride, and ethyl formate were distilled from calcium hydride after washing. All solvents were stored under nitrogen before use, after drying and distillation. Optical spectra were recorded on a Perkin-Elmer Lambda 20 instrument.

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(7) Hydrazine radical cations are examples of class III IV compounds that have large direct overlap between the charge-bearing units (they are directly bound), and very nonvertical transitions that have E_{op} much larger than 2H, as discussed in detail: Nelsen, S. F.; Tran, H. Q.; Ismagilov, R. F.; Ramm, M. T.; Chen, L.-J.; Powell, D. R. *J. Org. Chem.* **1998**, *63*, 2536.

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(9) Unfortunately, the radical cations of all the species we have seen that have had H determined by photoelectron spectroscopy are too unstable in solution to allow E_{op} measurement.

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(12) (a) We suggest that there has been confusion because of the habit of designating more than one band for transition metal-centered class III compounds as IV−CT bands. Only the lowest energy one is the Hush-IV band for which $E_{op} = 2H_{op}$. But the Hush-IV band is hardly observable for metal-centered compounds, such as the Creutz-Taube complex, because of their relatively small H values, caused by poor coupling of the ruthenium centers to the pyrazine (they appear in the IR region), as well as their low intensity. The higher energy bands that are easy to observe clearly involve much less charge transfer than typical metal, ligand charge transfer bands, and also clearly involve the bridge as well as metal-centered orbitals. Solvent effects for the higher energy bands of the Creutz−Taube complex and other class III compounds have been studied,[12b−d] but these studies do not address the question of whether H changes with solvent. (b) Creutz, C.; Chou, M. H. *Inorg. Chem.* **1987**, *26*, 2995. (c) Hupp, J. T.; Dong, Y. *Inorg. Chem.* **1994**, *33*, 4421. (d) Karki, L.; Williams, R. D.; Hupp, J. T. *Inorg. Chem.* **1998**, *37*, 2837.

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(14) (a) Interestingly, there is no correlation whatsoever for plots of H_{op} versus ET(30), a widely used empirical solvent polarity parameter based on E_{op} for the strongly endothermic ET induced by photolysis of a pyridinium phenoxide.[14b] The ordering of "solvent polarity" given by γ and by ET(30) is quite different for polar solvents. (b) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: Weinheim, 1988.

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(16) Solvent effects on E_{op} for class II compounds will be discussed elsewhere.

(17) We also tried other empirical fits, including using $(\epsilon_S)^{-1}$ and γ. Use of DN appears necessary to get any reasonable agreement. The best we could do without using $(n)^{-1/2}$ was H'_{op}(calcd) $= A' + B'$(DN) $+ D'(\epsilon_S)^{-1} + E'(\gamma)$. This equation has an additional fitting parameter compared to eq 1 and does not work for either CHCl$_3$ or THF for any of the compounds (deviations H_{op}(obsd) − H'_{op}(calcd) > 50 cm^{-1} for both solvents), but produces average deviations for the remaining eight solvents that are similar to those for eq 3, 12.3 for TMPD$^+$, 7.4 for k33)$_2$PD$^+$, and 9.7 for **TMB**$^+$.

(18) (a) Another solvent effect study on E_{op} for a Class III nitrogen-centered system was for a bis-bicyclic alkyl group protected 1,2,4,5-tetraaza-3,6-dioxa-cyclohexane radical cation.[18b] Its E_{op} values do not follow eq 1 or any other combination of solvent parameters we have examined. Its IV bands are asymmetric but do not show the clear vibrational fine structure of the compounds discussed in this paper. Its transition is presumably not as vertical. Because its charge-bearing hydrazines are doubly connected by single atoms (the carbonyl carbons), it seems very unlikely that this compound meets the criterion of negligible direct overlap for the charge-bearing units that is necessary for expecting the two state model prediction that $E_{op} = 2H$ to be accurate. (b) Nelsen, S. F.; Kim, Y.; Neugebauer, F. A.; Krieger, C.; Siegel, R. *J. Org. Chem.* **1991**, *56*, 1045.

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