J. Am. Chem. Soc. **1989**, *111*, 2045–2051

Solvent Effects on Self-Electron-Transfer Rate Constants for a Sesquibicyclic Hydrazine

Stephen F. Nelsen,* Yaesil Kim, and Silas C. Blackstock[†]

Contribution from the S. M. McElvain Laboratories of Organic Chemistry, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received April 25, 1988*

Abstract: Self-ET rate constants k_{et} were determined for $\mathbf{2},\mathbf{2}^{\bullet+}NO_3^-$ in 10 deuterated solvents over a range of temperatures using ^1H NMR line broadening. Values of $10^{-4}k_{et}$ determined in this work at 25 °C are the following: (perdeuterated) methanol, 0.06_8; ethanol, 0.2_2; 2-propanol, 0.3_2; nitromethane, 2.3_4; acetonitrile, 1.2_1; dimethyl sulfoxide, 1.0_4; dimethylformamide, 2.1_7; dichloromethane, 5.9_0; pyridine, 6.5_8; chloroform, 0.9_5. A plot of ln (k_{et}) at 25 °C versus the Marcus solvent parameter γ shows more scatter, even for the aprotic solvents, than do such plots for *p*-phenylenediamine derivatives. Plotting ln (k_{et}) versus the Kosower solvent parameter Z puts both aprotic solvents and alcohols on the same line and decreases the scatter. k_{et} in chloroform is anomalously low compared to the other solvents.

The rate constant for self electron transfer (ET), k_{et} in eq 1,

$$\mathrm{n} + \underline{\mathrm{c}} \overset{k_{et}}{\rightleftharpoons} \mathrm{c} + \underline{\mathrm{n}} \qquad (1)$$

between a neutral compound n and its cation radical **c** is of fundamental importance in Marcus theory of ET.[1,2] Knowledge of $\Delta G°$ for a "mixed" ET between n_1 and $\mathbf{c}_2$ and of self-k_{et} for both components allows direct calculation of the rate constant for ET in the mixed case, unless $\Delta G°$ is extremely negative. Although there is currently great interest in the "Marcus inverted region", where $\Delta G°$ is very negative and the rate constant for ET decreases as the reaction gets even more exothermic,[3] this paper will only address trying to understand the factors involved in self-ET, where $\Delta G°$ is zero. In Marcus ET theory,[1,2] solvated n,c pairs (considered to be near each other in solution but not yet having started toward the ET transition state) have a minimum energy structure, from which deviations may be considered to give rise to a parabolic energy well. Because electrons are far lighter than nuclei, ET will always be much more rapid than nuclear motions, and unless the solvated molecules undergoing ET are at the transition state, back-ET to give the starting materials will always occur. Marcus related the thermodynamics for relaxation upon ET with the kinetics for ET in the following manner. Completely vertical ET between ground-state reactants (simply taking an electron from n and transferring it to **c** without allowing relaxation of any sort) would give a highly destabilized product pair having the cation in neutral geometry (including the solvation shell), which we abbreviate **cng**, and the neutral compound in cation geometry, **ncg**. The energy gap from the n,c pair to the **cng**,**ncg** pair is called the Marcus λ value (shown graphically in Figure 1). The energy surface for the solvated product pair **c**,n has exactly the same shape as that for the reactant pair because self-ET is being considered, but is displaced along the horizontal axis which represents the reaction coordinate. The barrier to thermal electron transfer between **n** and **c** is pictorially represented by the point at which the parabolas cross (assuming no charge-delocalized intermediate of lower energy occurs), which is one-fourth of the vertical energy gap λ because of the geometric properties of parabolas. The vertical energy gap λ is broken into inner- and outer-shell terms, inner corresponding to energy changes which occur within the n and **c** molecules, and outer to those which occur in the solvent surrounding these molecules, giving eq 2 (we can ignore the

$$\Delta G^*_{et} = (\lambda_i + \lambda_o)/4 \qquad (2)$$

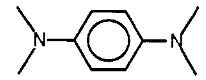
electrostatic work term here, because it is zero for the n,c ET to which we limit this discussion). The resolvation, or outer-shell term λ_o, will be sensitive to the distance between n and **c** at the transition state, and is numerically evaluated using eq 3, in which

$$\lambda_o = 332.4(\text{distance parameter})\gamma \qquad (3)$$

332.4 is the constant required if the energy λ_o is in kcal/mol and distances in the distance parameter $g(r,d)$ are in Å,the units we employ in this paper. The Marcus solvent polarity parameter γ is defined in eq 4, where n_D is the refractive index, and ϵ the

$$\gamma = (1/n_D{}^2 - 1/\epsilon) \qquad (4)$$

dielectric constant of the solvent employed. γ is intended to represent the effect of changing solvent on stabilizing the transition state and ground-state molecules. Grampp and Jaenicke[4] have recently carried out a detailed study of self-ET for tetramethyl-*p*-phenylenediamine (**1**) n,c pairs (as well as five analogues which basically gave similar information) in six solvents at various temperatures and gave a detailed Marcus analysis of their data. We shall refer to this work as GJ for brevity, and use it to represent previous work on organic ET reactions[2] which give "fast" k_{et} values, above 10^8 M^{-1} s^{-1}. It was decided long ago[1,5] that self-ET in "fast" k_{et} compounds such as **1** was dominated by the outer-shell (resolvation) term λ_o.



1

Results

Because eq 1 is always at equilibrium under ordinary conditions, measurement of k_{et} for self-ET has relied upon magnetic resonance line-broadening experiments. ET exchanges an electron without flipping nuclear spins, which affects the magnetic resonance spectrum observed if the rate of exchange is fast enough. The broadening of lines in the ESR spectrum of **c** has usually been used to measure k_{et} for organic compounds, because k_{et} is normally above about 10^8 M^{-1} s^{-1}, and the ESR time scale is appropriate for observing the broadening caused by ET. Significant ESR line

---

[†] Current address: Department of Chemistry, Vanderbilt University.

(1) For reviews by Marcus, see: (a) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (b) Marcus, R. A. *Special Topics in Electrochemistry*; Rock, P. A., Ed.; Elsevier: Amsterdam, 1977; p 161.

(2) For a review of applications to organic chemistry, see: Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79.

(3) See, for example: (a) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047. (b) Miller, J. R.; Beitz, J. V.; Huddleston, R. K. *Ibid.* **1984**, *106*, 5057. (c) McLendon, G.; Miller, J. R. *Ibid.* **1985**, *107*, 7811. (d) Eriksen, J.; Jorgensen, K. A.; Linderberg, J.; Lund, H. *Ibid.* **1984**, *106*, 5083.

(4) (a) Grampp, G.; Jaenicke, W. *Ber. Bunsenges. Phys. Chem.* **1984**, *88*, 325. (b) Grampp, G.; Jaenicke, W. *Ibid.* **1984**, *88*, 335. (c) Grampp, G.; Jaenicke, W. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 1035.

(5) (a) Marcus, R. A. *J. Chem. Phys.* **1957**, *26*, 872. (b) Hale, J. M. *Reactions of Molecules at Electrodes*; Hush, N. S., Ed.; Wiley: New York, 1971; Chapter 4.

0002-7863/89/1511-2045$01.50/0

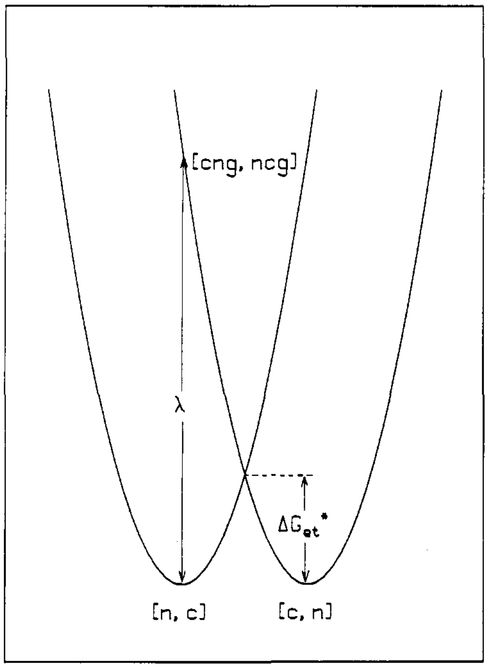


Figure 1. Marcus diagram for a self-ET reaction.

Table I. $\mathbf{2,2^{\bullet+}NO_3^-}$ Self-ET Kinetics at 25 °C

solvent	code[a]	$10^{-4}k_{et}$[b]	γ	τ_L[c]	Z[d]
CD_3OD	A	0.06_8	0.538	3.3	83.6
C_2D_5OD	B	0.2_2	0.500	15.4	79.6
C_3D_7-2-OD	C	0.3_2	0.474	54.0	76.3
CD_3NO_2	D	2.3_4[e]	0.498	0.22	72.1[f]
CD_3CN	E	1.2_1[g]	0.528	0.2	71.3
$(CD_3)_2SO$	F	1.0_4[h]	0.438	2.36	71.1
$(CD_3)_2NCDO$	G	2.1_7	0.464	1.32	68.5
CD_2Cl_2	H	5.9_0	0.380	0.8	64.2
CD_2Cl_2		2.5_1[i]			
C_5D_5N	J	6.5_8	0.359	1.23	64.0
$CDCl_3$	K	0.9_5[j]	0.268	2.2	63.2

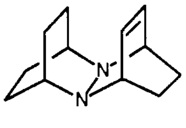
[a] Used to identify solvents in the figures. [b] Units for k_{et}, $M^{-1}\ s^{-1}$. [c] Units, 10^{-12} s. [d] Units, kcal/mol. [e] Average of two runs with $10^{-4}k_{et}$ values of 2.25 and 2.44. [f] Estimated from the E_T value; see text. [g] Average of five runs with $10^{-4}k_{et}$ values of 1.33, 1.02, 1.32, 1.02, and 1.38. [h] Average of two runs with $10^{-4}k_{et}$ values of 1.02 and 1.06. [i] For $\mathbf{2^{\bullet+}OTs^-}$. [j] Average of two runs with $10^{-4}k_{et}$ values of 1.01 and 0.89.

Table II. $\mathbf{2,2^{\bullet+}NO_3^-}$ Self-ET Activation Parameters

solvent	code	$\Delta H^{\ddagger}$[a,b]	$\Delta S^{\ddagger}$[b,c]	$-T\Delta S^{\ddagger}/\Delta G^{\ddagger}$[d]
CD_3OD	A	7.4 (10)	−21 (3)	0.45
C_2D_5OD	B	9.0 (6)	−13 (2)	0.30
C_3D_7-2-OD	C	9.6 (3)	−10 (1)	0.24
CD_3NO_2	D	8.7 (6)	−9 (2)	0.24
CD_3CN	E	7.4 (5)	−15 (2)	0.38
$(CD_3)_2SO$	F	6.7 (9)	−18 (3)	0.44
$(CD_3)_2NCDO$	G	6.4 (2)	−17 (1)	0.45
CD_2Cl_2	H	7.4 (5)	−12 (2)	0.32
(CD_2Cl_2)[e]		[7.1 (3)]	[−15 (1)]	(0.39)
C_5D_5N	J	6.3 (2)	−15 (1)	0.42
$CDCl_3$	K	8.3 (8)	−13 (3)	0.31

[a] In kcal/mol. [b] Numbers in parentheses are statistical error derived from the straightness of the line in the Eyring plot, calculated at the 95% probability level, in the last place quoted. [c] In cal/deg·mol. [d] At 25 °C. [e] For $\mathbf{2^{\bullet+}OTs^-}$.

broadening is observed for k_{et} values above about $10^6\ M^{-1}\ s^{-1}$.



2

Our work has focused on the study of ET in hydrazines,[6] where the geometry change upon electron loss is unquestionably large and k_{et} far smaller than for **1**. No ESR line broadening is shown by hydrazine n,c mixtures because k_{et} is too small. The NMR time scale is about 10^3 times that of ESR, allowing NMR line broadening to be used to measure smaller k_{et} values than ESR. Special structures limiting geometry change must be employed to make k_{et} for hydrazines fast enough to allow its measurement even by NMR, but we found that the n,c ET of **2** is especially convenient for quantitative study.[7] Both n and c are isolatable in pure form, and k_{et} is of appropriate size for measurement by ^1H NMR in the slow exchange region, where theory for extracting k_{et} is remarkably simple. Electron-exchange line broadening for **2** can be accurately determined for the vinyl protons, which show narrow lines analyzable as the AA′ portion of an AA′XX′ system in the unbroadened spectrum. In this work we report a detailed study of the effect of solvent and temperature on k_{et} for self-ET of $\mathbf{2,2^{\bullet+}NO_3^-}$. Support for the statement that mixtures of **2** and $\mathbf{2^{\bullet+}NO_3^-}$ are in the slow exchange region, where exchange broadening ν is related to k_{et} by eq 5, has been previously pub-

$$k_{et} = \pi\Delta\nu[c]^{-1} \qquad (5)$$

lished.[8] Values determined for k_{et} in 10 perdeuterated solvents at 25.0 °C are listed in Table I. It was previously shown[7] that $\Delta\nu$ is directly proportional to the $\mathbf{2^{\bullet+}}$ concentration, and in this work temperature was varied at a single $\mathbf{2^{\bullet+}}$ concentration. In order for eq 5 to be valid, the concentration of **2** must greatly exceed that of $\mathbf{2^{\bullet+}}$ (eq 5 is for pseudo-first-order conditions), and it was noted in this work that k_{et} values derived using eq 5 change noticeably if their ratio does not exceed 10. The $\mathbf{2^{\bullet+}}$ concentrations and $\mathbf{2/2^{\bullet+}}$ ratios used appear in the Experimental Section; ratios for all experiments used are above 25. All k_{et} (25 °C) values were obtained by interpolation of data collected at three to six temperatures (see Experimental Section). Perdeuterated solvents were employed because FT ^1H NMR was used to determine $\Delta\nu$, and protons in the solvent cause dynamic range difficulties. A data set was collected using unlabeled CH_3CN as solvent, in which the single solvent peak was suppressed by proper choice of data collection parameters. It gave k_{et} of $1.20 \times 10^4\ M^{-1}\ s^{-1}$, close to the $1.21 \times 10^4\ M^{-1}\ s^{-1}$ average of five runs in CD_3CN, so it does not appear that k_{et} is significantly sensitive to the presence of deuterium in the solvent. We are not as sure that the solvent physical parameters also included in Table I are the same for deuterated as for unlabeled solvent, but we have used values for unlabeled material, as they are the only ones available. The presence of 0.03% Me_4Si in the $CDCl_3$ sample originally used was found not to influence k_{et} significantly; $10^{-4}k_{et}$ values of 1.01 and 0.89 (±6% from the mean) were determined with and without Me_4Si in the sample. We were unable to get enough $\mathbf{2^{\bullet+}NO_3^-}$ to dissolve in CCl_4, THF (tetrahydrofuran), DME (1,2-dimethoxyethane), dioxane, or acetone to include them in this study.

The reproducibility of the k_{et} values determined for **2** is not as high as the good precision for measuring $\Delta\nu$ would predict. We believe the problem is principally caused by the difficulty in purifying $\mathbf{2^{\bullet+}}$ salts. The presence of other materials in a $\mathbf{2^{\bullet+}}$ salt sample used for kinetic measurements would lead to a reported k_{et} value that is too low. The presence of air in the samples could produce extra $\mathbf{2^{\bullet+}}$ and give reported k_{et} values that are too high. We have had trouble with reproducibility for the CD_3CN runs (Table I, footnote *g*). We are not sure why we obtained significantly lower numbers twice out of the five runs made, and although we suspect impure cation radical, and hence that the real number is the higher value, we have used the average of the five runs in the discussion which follows. Although the precision in

---

(6) For a review see: Nelsen, S. F. *Molecular Structures and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: Deerfield Beach, FL, 1986; Vol. 3, pp 1–86.

(7) Nelsen, S. F.; Blackstock, S. C. *J. Am. Chem. Soc.* **1985**, *107*, 7189.

(8) Nelsen, S. F.; Blackstock, S. C.; Kim, Y. *J. Am. Chem. Soc.* **1987**, *109*, 677.

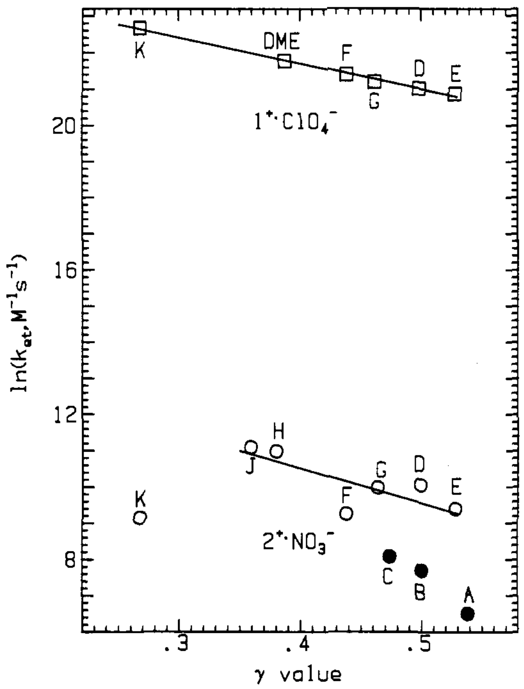


Figure 2. Plot of ln (k_{et}) versus γ for **1** and **2**. For identification of the solvents, see Table I (solvents for **1** were not deuterated; those for **2** were). Filled circles are for alcohols.

measuring k_{et} appears to usually be better than ±5%, the absolute accuracy of the numbers reported in Table I may not be better than 15%.

Activation parameters obtained from Eyring treatments of the data are shown in Table II. Straight lines with correlation coefficients r of −0.999 were found for all ln (k_{et}/T) versus $1/T$ plots except that for the smallest k_{et} solvent, CD_3OD, where r was −0.995. Statistical errors in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are included in Table II. The observed $\Delta\nu$ values are, of course, smallest for CD_3OD (0.8 to 5.1 Hz), which would magnify errors in determining $\Delta\nu$. Observed $\Delta\nu$ values ranged from 3.4 to 25.3 Hz for the next slowest k_{et} case, C_2D_5OD. The data of Table II have not been corrected for solvent volume change as the temperature is varied. This effect has been shown to be rather small. Using published temperature coefficients for solvent expansion[9] for CH_3CN and C_2H_5OH, $\Delta H^{\ddagger}$ is calculated to increase 0.2 kcal/mol and $\Delta S^{\ddagger}$ to become 0.7 eu less negative when solvent expansion is taken into account. These changes are certainly smaller than we can interpret, and we have not done similar corrections on the other data, for which the necessary expansion temperature coefficients are often lacking anyway.

Almost all of this work was for the NO_3^- salt of $\mathbf{2}^{\cdot+}$, but similar data for the tosylate salt were obtained in CD_2Cl_2 (ε 8.9), and the NO_3^-/OTs^- salt k_{et} ratio at 25 °C was measured at 2.3_5; see Tables I and II. This agrees qualitatively with data for this ratio reported previously[7] in $CDCl_3$ (ε 4.7), where the rate ratio was 2.2 (at slightly different temperatures, 23.0 and 24.8 °C, respectively). The rates for these two salts are experimentally indistinguishable in the significantly more polar solvent $(CD_3)_2SO$ (ε 46.7).[7]

Discussion

Figure 2 compares ln (k_{et}) versus γ plots for the GJ data[4a] on $\mathbf{1,1}^{\cdot+}ClO_4^-$ at 20 °C with that of Table I for $\mathbf{2,2}^{\cdot+}NO_3^-$ at 25 °C. Self-ET for **1** is about 10^5 times more rapid for **1** than for **2** in acetonitrile at room temperature. We shall use the transition-state-theory interpretation of rate constants throughout this paper and equate the Marcus barrier λ with $4\Delta G^{\ddagger}$. The corresponding Marcus λ values calculated at 25 °C in acetonitrile from the GJ temperature variation data[4b] are 19.6 kcal/mol for **1**, and from Table I, 47.6 kcal/mol for **2**. The qualitative reason for the 2.4-fold larger λ value of **2** is clearly the larger size of the λ_i term of the hydrazine. The GJ data for k_{et} of **1** in six aprotic solvents correlate very well with γ (squares in Figure 2), the average ln (k_{et}) deviation being 0.04, and the ln (k_{et}) versus γ slope, $\beta = -7.0$. The plot for **2** shows considerably more scatter. The data for the three hydroxylic solvents studied (A–C, plotted as filled circles in Figure 2) must be eliminated from quantitative consideration in such a plot because γ clearly does not describe hydroxylic solvent polarity adequately, presumably because of hydrogen-bonding effects.[1] Chloroform (K), the least polar solvent we were able to study for **2**, shows a distinctly smaller ln (k_{et}) value than its γ value predicts (which it should be noted does not occur for **1**), and we shall also temporarily eliminate this point from consideration. The other six aprotic solvents studied, nitromethane (D), acetonitrile (E), dimethyl sulfoxide (F), dimethylformamide (G), methylene chloride (H), and pyridine (J), still give a poorer correlation with γ than do the GJ data for **1**. The average deviation of ln (k_{et}) is 0.31, $r = -0.78$, and $\beta = -9.1$. The dimethyl sulfoxide point (F) is by far the largest deviator and the average deviation drops to 0.13, $r = -0.97$ ($\beta = -9.5$), if this point is simply eliminated, but this is still three times the average deviation found for compound **1**. The low k_{et} compound **2** does not give nearly as good a ln (k_{et}) correlation with γ as does the high k_{et} compound **1**.

Because the inner-shell term λ_i only represents effects within n and **c**, it should be independent of solvent. We note that although λ for large k_{et} compounds like **1** is supposed to be dominated by the outer-shell (resolvation) term λ_o and that for **2** dominated by the inner-shell (internal geometry change) term λ_i, rather similar β values are observed for **1** and **2**, although there is admittedly a lot of scatter in the plot for **2**. The ln k_{et} versus γ slope, β, is proportional to the distances parameter $g(r,d)$ of eq 3 according to eq 6. As GJ points out,[4a] eq 6 gives $g(r,d) = 0.0491$ Å^{-1} for

$$\beta = \frac{332.4}{4RT} g(r,d) \qquad (6)$$

1. If the self-ET transition state is modeled as two charged spheres of radius r which just touch, the distance d between the centers of the spheres is $2r$. Although $g(r,d)$ is usually given as $1/2r$ in this touching spheres model, GJ quote the complete solution as a function of d, for which $g(r,d) = 0.94/2r$ when $d = 2r$. Thus $r = 9.57$ Å in the touching spheres model for **1** self-ET, which is larger than the molecular dimensions of **1**. **1** is quite far from being spherical, however. The X-ray structure for $\mathbf{1}^{\cdot+}ClO_4^-$ was used to estimate the transition-state components as ellipsoids with axes 11.00:5.90:3.10 Å, 3.55:1.91:1 ratios.[4a] Solution of the equation for $g(r,d)$ using this ellipsoid gave $g(r,d) = 0.0537$ Å^{-1} at a d value of 5.46 Å, the distance between the centers of the rings in the X-ray structure of $\mathbf{1}^{\cdot+}ClO_4^-$. GJ concluded that eq 3 and 6 do quantitatively describe solvent effects on self-ET of **1**, and that its transition state for ET resembles the "π-stacked" geometry of crystalline $\mathbf{1}^{\cdot+}$.[4]

A similar treatment of β for self-ET of **2** gives $g(r,d) = 0.068$ Å^{-1}, $r = 7.2$ Å, which is also considerably larger than the molecular dimensions of **2**. The X-ray structure of neutral **2** would fit in a box of dimensions a:b:c 7.20:5.15:4.69 Å, calculated from the average of the H,H positions indicated in Figure 3 plus 0.70 Å, twice the van der Waals radius of H. Calculated in the same way, $\mathbf{2}^{\cdot+}$ would fit in a 7.00 × 5.19 × 4.80 Å box. The ratios of the dimensions estimated for the hydrazine components of the transition state of **2** self-ET (halfway between those of n and of **c**) are 1.5:1.1:1. **2** is substantially more spherical than is **1**, and we do not believe that the discrepancy between the radius obtained from β and that of the molecule can be attributed to deviation from a spherical shape. Equations 3 and 6 do not quantitatively give a reasonable self-ET transition-state distance for **2**, which would have to show a β value twice as large to produce a radius the size of half the largest dimension of **2** using these equations. A significant resonance stabilization for a charge-delocalized intermediate between the n,**c** starting material and the **c**,n product

---

[9] Dean, J. A. *Lange's Handbook of Chemistry*, 12th ed.; McGraw-Hill: New York, 1979; pp 10–127.

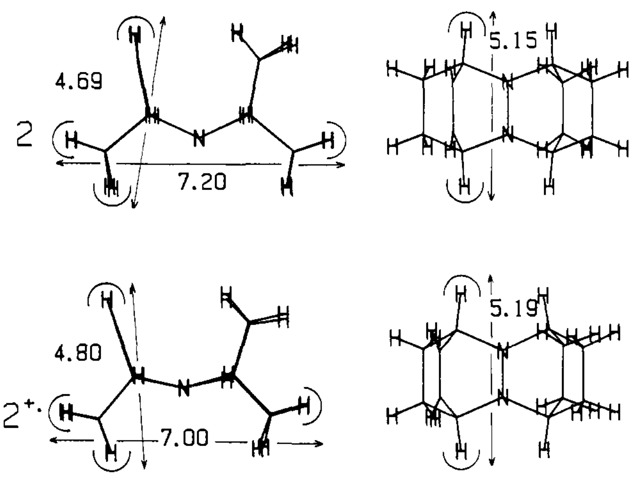


Figure 3. Projections of line drawings of the X-ray crystal structures for **2** and $\mathbf{2}^{\bullet+}$ showing how the dimensions of these molecules were obtained. Distances are in Å.

of self-ET in **2** would cause these equations to break down. Although charge-delocalized 3e σ-bonded structures are known to occur between the cation radicals and neutral form of some trialkylamines, there is no experimental evidence for such behavior, even intramolecularly, in hydrazines.[8] Furthermore, the tetraalkylhydrazine cation radical 3e π-bond resonance energy has been found to be larger than the 3e σ-bond resonance energy for diamine cation radicals.[6] We suggest that **2** is the best organic candidate for testing eq 3 and 6 which has been reported, because the molecule is nearly spherical, and k_{et} is small enough that the value observed does not require a diffusion correction before comparison with theory. As a result of this test, we believe that the numerical accuracy of eq 3 and 6 has to be seriously questioned. Most organic molecules deviate far more from a spherical shape than **2**, and its does not seem to us to be particularly reasonable to attempt to quantitate the λ_0 effect by including dependence on the distance between two touching spheres, which is almost universally inapplicable.

More recent treatments of ET theory, especially those of Sutin,[10] have explicitly introduced formation of encounter or charge-transfer complexes prior to electron transfer, which were neglected in the original treatment. The presence of such complexes cause an equilibrium constant to be introduced in the preexponential term of the rate equation. We do not doubt the presence of encounter complexes in ET reactions, but do not see any reason to believe that **n**,**c** pairs from **2** would form tighter encounter complexes than those formed for fast ET compounds like **1**. Such prior complexation should be more important for less sterically hindered molecules, which can bring a larger portion of their surfaces into contact. The gas-phase dimer cation radical formation enthalpy for tetramethylhydrazine has been measured[11] at 13.0 kcal/mol, which is somewhat less than the 16 ± 1 kcal/mol observed in the gas phase for substituted benzenes.[12] We would expect smaller values in the gas phase for the more sterically hindered **2**. Considerably smaller encounter complex stabilizations than these will occur in solution, where **c** has other possibilities besides n for achieving solvation. We are unable to quantitatively evaluate how encounter complexation would vary with solvent, and cannot address the question of whether such complexes might be responsible for the failure of eq 3 and 6 to give a reasonable value of *d* for **2**.

The role of solvent dynamics in ET processes has recently been emphasized by Calef and Wolynes, Weaver, Kapturkiewicz, and others.[13] Although solvent thermal reorientation and dielectric relaxation doubtless are important for high k_{et} compounds, we do not see any way that they could be more important for low k_{et} compounds like **2**. We have nevertheless included in Table I the longitudinal dielectric relaxation times, τ_L, which vary widely for the solvents studied, and have examined our data to look for dependence upon solvent dynamics. Treatments of Weaver and of Kapturkiewicz have predicted a linear plot of ln $(k_{et})\tau_L(\gamma)^{-1/2}$ versus γ if solvent dynamics dominates the rate constant. Our data certainly do not follow this equation, and *r* for such a plot is only 0.71 (excluding the $CDCl_3$ point).

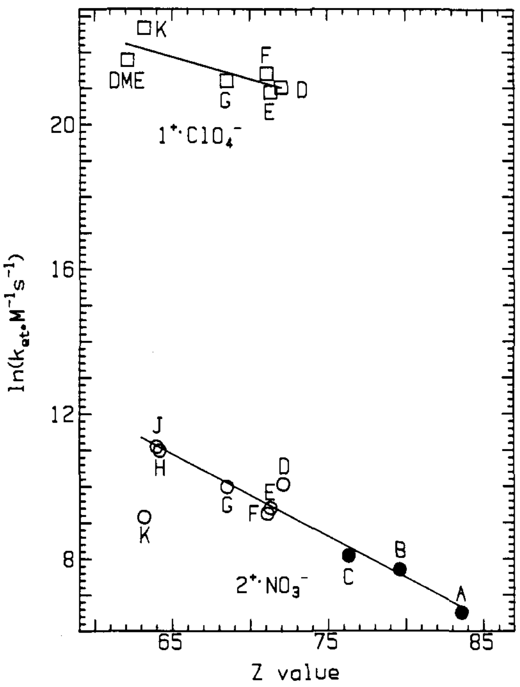
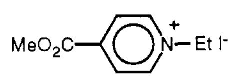
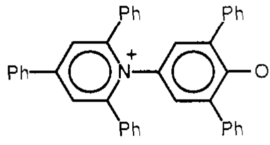


Figure 4. Plot of ln (k_{et}) versus *Z* for **1** and **2**. For identification of the solvents, see Table I (solvents for **1** were not deuterated; those for **2** were). Filled circles are for alcohols.

Taking a different tack to considering the k_{et} values of Table I, we turn to an old standby of physical organic chemists, Kosower *Z* values,[14] which are the electronic transition energy for the charge-transfer band of 1-ethyl-4-carbomethoxypyridinium iodide, **3**, in kcal/mol. Kosower showed that *Z* does correlate with



3



4

experimental rate data for S_N1 solvolysis, and *Z* has proven quite useful for correlating solvent effects on rates of ionic reactions. Dimroth and co-workers[15] introduced the conceptually identical E_T values, which use transition energies for zwitterion **4**. **4** is

---

(10) (a) Marcus, R. A.; Sutin, N. *Inorg. Chem.* **1975**, *14*, 213. (b) Brunschwig, B. S.; Logan, J.; Newton, M. D.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 5798. (c) Marcus, R. A. *Int. J. Chem. Kinet.* **1981**, *13*, 865.

(11) Nelsen, S. F.; Rumack, D. T.; Meot-Ner (Mautner), M. *J. Am. Chem. Soc.* **1987**, *109*, 1373.

(12) Meot-Ner (Mautner), M.; Hamlet, P.; Hunter, E. P.; Field, F. H. *J. Am. Chem. Soc.* **1978**, *100*, 5466.

(13) (a) Calef, D. F.; Wolynes, P. G. *J. Phys. Chem.* **1983**, *87*, 3387. (b) Calef, D. F.; Wolynes, P. G. *J. Chem. Phys.* **1983**, *78*, 470. (c) Aleksandrov, I. V.; Gol'danskii, V. I. *J. Chem. Phys.* **1984**, *87*, 455. (d) Kapturkiewicz, A.; Behr, B. *J. Electroanal. Chem.* **1984**, *179*, 187. (e) Zhang, X.; Leddy, J.; Bard, A. J. *J. Am. Chem. Soc.* **1985**, *107*, 3719. (f) Weaver, M. J.; Gennett, T. *Chem. Phys. Lett.* **1985**, *113*, 213. (g) Gennett, T.; Milner, D. F.; Weaver, M. J. *J. Phys. Chem.* **1985**, *89*, 2787. (h) Harrer, W.; Grampp, G.; Jaenicke, W. *Chem. Phys. Lett.* **1984**, *112*, 263.

(14) (a) Kosower, E. M. *J. Am. Chem. Soc.* **1958**, *80*, 3253. (b) Kosower, E. M. *Molecular Biochemistry*, McGraw-Hill: London, 1962; pp 180–195.

(15) (a) Dimroth, K.; Reichardt, C.; Siepmann, T.; Bohlman, F. *Justus Liebigs Ann. Chem.* **1963**, *661*, 1. (b) Reichardt, C. *Ibid.* **1971**, *752*, 64. (c) Reichardt, C. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 29. (d) E_T does shift away from *Z* at the low polarity end. We have really used E_T values for nitromethane and hexane, but cast them in terms of *Z* using eq 7.

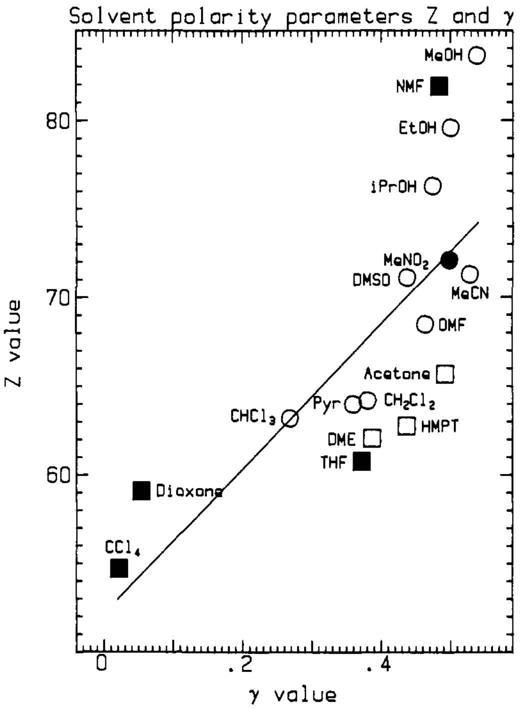


Figure 5. Plot for Z versus γ. NMF is $CH_3NHC({=}O)H$, HMPT is $((CH_3)_2N)_3PO$. The circles represent the solvents used in Tables I and II, and the filled figures employ Z values estimated from E_T values using eq 7.

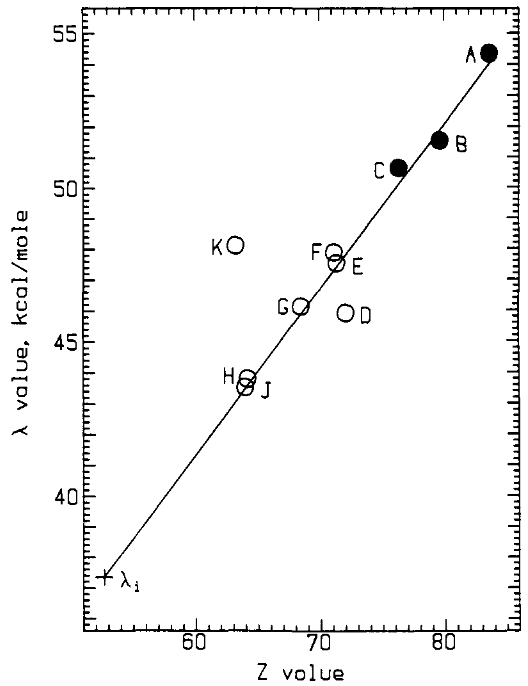


Figure 6. Plot of λ (using $\lambda = 4\Delta G^{*}_{\mathrm{et}}$) versus Z for the data of Table I. (Value for $CDCl_3$ was not used in drawing the regression line.)

soluble in a wider range of solvents and shows a linear plot with Z, as given in eq 7,[15c] which was used to estimate Z for nitro-

$$Z = 1.259E_{\mathrm{T}} + 13.76 \qquad (7)$$

methane in Table II, as it was not in Kosower's solvent set. Figure 4 shows a plot of our data for **2** along with that of GJ for **1** versus Z. Except for the chloroform point (which lies far off the line as it does in the correlation with γ), the plot for **2** is reasonably linear, average deviation 0.20, $r = -0.979$.[16a] This is especially noteworthy because the three alcohols correlate with the aprotic solvents. Strong enough hydrogen bonding to the neutral component in an ET reaction should decrease the rate, but Z for **3** and E_{T} for **4** show a linear correlation with each other for both hydroxylic and nonhydroxylic solvents, indicating that hydrogen-bonding effects on λ for both the iodide anion of **3** and the hindered phenoxide of zwitterion **4** are not extremely different. Figure 4 indicates that λ for self-ET of **2** is influenced quantitatively the same as λ for the substantially more endothermic charge transfer in **3**. A tetra-α-branched hydrazine such as **2** would not be expected to form especially strong hydrogen bonds anyway.

We note that the CT transition energies of Z and E_{T} are direct experimental measurements of the dependence of the Marcus λ value for **3** and **4** upon solvent. Back-ET occurs rapidly for these cases, of course, because it is quite exothermic for the iodine atom, pyridyl radical pair produced from **3** and the phenoxy radical, pyridyl diradical produced from **4**. The question of how well Z correlates with the Marcus solvent parameter γ, which is supposed to quantitatively describe how λ values in general vary with solvent should be asked, if γ is going to be used to quantitatively describe solvent effects. The plot of Z versus γ shown in Figure 5 demonstrates that these two sets of numbers are actually rather different; their correlation coefficient for the 10 solvents used in this work is only 0.81, and for the 17 solvents of Figure 5, 0.74. The fact that Z correlates much better with E_{T} indicates that solvent effects on λ are similar for the ion pair **3** and the intramolecular zwitterion **4**. We emphasize that γ does not quantitatively describe the effect of changing solvent on λ for these systems, and that use of Z allows consideration of protic as well as aprotic solvents for **2**.

Equation 3 states that λ_{o}, the resolvation contribution to the Marcus ET barrier λ, drops to zero in very poorly solvating solvents. λ_{i} can therefore be separated from λ_{o} by extrapolation of λ to $\gamma = 0$, which ought to work whether or not eq 3 and 6 quantitatively calculate the distance at the ET transition state. Doing this for GJ's data on **1** gives for acetonitrile at 20 °C $\lambda_{\mathrm{i}} = 11.5$ kcal/mol (58% of the observed λ value), $\lambda_{\mathrm{o}} = 8.5$ (42% of λ). Even for **1**, then, the dependence of k_{et} on solvent indicates that over half of the observed barrier is caused by internal reorganization, the λ_{i} term. This is a qualitatively rather different result from the often repeated statement that λ_{o} dominates "fast" self-ET reactions of organic compounds. An analogous extrapolation using the Z value dependence of λ has been carried out by extrapolation to $Z = 52.6_6$, the value calculated for hexane using its measured E_{T} value and eq 7.[15] We argue that doing this is equivalent to extrapolating to $\gamma = 0$, because $\gamma = 0.003$ for *n*-hexane. Figure 6 shows a plot of the data for **2**. The regression line for the nine solvents (including the alcohols), excluding $CDCl_3$, has an r value of -0.978, average deviation in $\lambda = 0.5$ kcal/mol.[16b] The λ value at $Z = 52.6_6$ gives $\lambda_{\mathrm{i}} = 37.3$ kcal/mol, and therefore $\lambda_{\mathrm{o}} = 10.2$ kcal/mol for acetonitrile at 25 °C, corresponding to 21% of the observed λ value of 47.5 kcal/mol. Use of the correlation with Z allows including the data measured in alcohols, substantially extending the effective polarity range studied, and presumably improving the accuracy of the extrapolation to extremely nonpolar solvent which the λ_{i} value represents. Using λ_{i} of 37.3 kcal/mol, λ_{o} increases from 6.2 for pyridine to 17.0 for methanol, and the slope of the λ_{o} versus Z plot is 0.54 kcal/mol. Similar treatment of the GJ data for **1** gives a poorer linear correlation ($r = -0.820$), as it must because these data give a very straight line in the correlation of ln (k_{et}) with γ. It gives λ_{i} of 14.1 kcal/mol and $\lambda_{\mathrm{o}} = 5.9$ kcal/mol for acetonitrile, 29% of the observed λ value of 20.0 kcal/mol at 20 °C.

We note that k_{et} for **2** in $CDCl_3$ is distinctly lower than that predicted by either γ or Z, in contrast to the behavior observed by GJ for **1**, where the chloroform point falls on the line.

---

(16) (a) The nitromethane point (D) is the largest deviator. Eliminating it, the average ln (k_{et}) deviation is 0.11, $r = 0.997$. (b) The similar plot of λ versus E_{T} is very similar, $r = 0.970$, average deviation in λ 0.5$_5$ kcal/mol, λ_{i} value from the extrapolated value for *n*-hexane ($E_{\mathrm{T}} = 30.9$), 36.7 kcal/mol, λ_{o} for acetonitrile 10.8 kcal/mol, 23% of λ.

Something is clearly different about this solvent for self-ET of **2**. Hydrogen bonding as a cause for the low k_{et} value seems to be ruled out by the lack of such effects in Figure 4 for alcohols, which are clearly better at hydrogen bonding than is chloroform. **2** is extremely easily oxidized, and chloroform is relatively easy to reduce, so perhaps some special charge-transfer interaction is present. This was the reason for including nitromethane in our set of solvents, as it is even more easily reduced than is chloroform. Although the point for nitromethane is farthest from the line shown in Figure 4 except for chloroform, its deviation is in the opposite direction, which makes it seem unlikely that it is the reducibility of chloroform which is responsible for its anomalous behavior. Chloroform is the lowest polarity solvent in which we were able to dissolve enough $\mathbf{2}^{\bullet+}NO_3^-$ to measure k_{et}, yet it dissolves the salt easily. The solvated anion must also be transferred at the transition state if it is not completely solvated and far away from the cation and neutral. Presumably if ion pairing were tight enough, the anion might be required to lie physically near both hydrazine partners, tending to pry them apart, which would lower the rate of ET. There doubtless is ion pairing in chloroform, because the rate constant observed is somewhat counterion dependent. Nevertheless, the counterion effect on k_{et} is similar in chloroform and in methylene chloride, yet methylene chloride does not show a decreased rate constant compared with more polar solvents, while chloroform obviously does.

We shall now address the decomposition of $\Delta G^{\ddagger}_{et}$ into $\Delta H^{\ddagger}_{et}$ and $\Delta S^{\ddagger}_{et}$ given in Table II. We previously discussed in detail the estimation of λ_i from the **cng,ncg** to n,c relaxation energy using semiempirical MO calculations employing Dewar's AM1 program.[8] These calculations gave $\lambda_i/4$ of 2.06 kcal/mol for **1**, compared with the observed $\Delta H^{\ddagger}_{et}$ value of 2.63 kcal/mol, and 8.21 for the symmetrical molecule obtained by reducing the double bond of **2**. $\Delta H^{\ddagger}_{et}$ for the saturated molecule could not be obtained because of decomposition difficulties, but k_{et} is about $^1/_{15}$th that of **2** at 23 °C.[8] AM1 calculations give a slightly higher $\lambda_i/4$ value for **2** of 8.40 kcal/mol (experimental $\Delta H^{\ddagger}$ = 7.3 kcal/mol in acetonitrile, but a range from 6.3 to 9.6 kcal/mol was found in the 10 solvents studied; Table II). The shapes of both **2** and $\mathbf{2}^{\bullet+}$ obtained from these AM1 calculations are quite similar to those from the X-ray structures, but the molecular dimensions obtained as in Figure 3 are about 5% larger; for **2**, 7.47:5.45:4.90 Å, and for $\mathbf{2}^{\bullet+}$, 7.39:5.48:4.90 Å. For comparison, one-fourth of the value of λ_i estimated from the plot of λ versus Z (Figure 6) is 9.3_3 kcal/mol. $\Delta S^{\ddagger}_{et}$ values, which contribute significantly to the rate, have not been considered here, and we do not know how to quantitatively estimate them for either the inner- or outer-sphere reactions.

It will be noted that the $\Delta S^{\ddagger}_{et}$ values observed for **2** are quite negative, ranging from −9 to −17 eu. A significant fraction of this negative entropy arises from the fact that **2** and $\mathbf{2}^{\bullet+}$ must collide to allow electron transfer. Use of the formula quoted by GJ (ref 4b, eq 9) for $\Delta S_0^{\ddagger}$ for touching of two hard spheres with diameters of 7.10 and 4.75 Å (the largest and smallest molecular dimensions estimated above for the transition state in **2** self-ET), gives values of −6.4 and −8.0 eu, respectively. From the GJ activation parameters[4b] for **1** self-ET, k_{et} is 1.60 × 10^9 M^{-1} s^{-1} at 25 °C (1.46 × 10^9 at 293 K, compared with 1.17 × 10^9 reported for the single temperature measurement at 293 K[4a]), so from Table II, **1** has a k_{et} value 1.37 × 10^5 times that of **2** at 25 °C, a factor of 2660 arising from the lower $\Delta H^{\ddagger}_{et}$ and of 52 from the less negative $\Delta S^{\ddagger}_{et}$ of **1** compared to **2**. Both enthalpy and entropy of activation determined for **2** are rather solvent sensitive, the highest and lowest values differing by 33 and 47%, respectively (eliminating the data for CD_3OD, which as pointed out above are rather less accurate than the rest because k_{et} was inconveniently small). Figure 7 shows $\Delta H^{\ddagger}$ and $T\Delta S^{\ddagger}$ as a function of Z value, with statistical error bars for the points. We cannot explain the variation of the relative contribution of $\Delta H^{\ddagger}$ and $T\Delta S^{\ddagger}$ to $\Delta G^{\ddagger}$. Despite the relatively low statistical error, we are as a result somewhat concerned about the accuracy of our decomposition of the free-energy barrier into $\Delta H^{\ddagger}_{et}$ and $\Delta S^{\ddagger}_{et}$. The 40° temperature range we were typically able to use is not very large, and separation of $\Delta G^{\ddagger}$ into $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ using magnetic resonance data has often been a problem in conformational work. We have no good way of estimating what systematic errors might be. It should be noted that GJ found an even larger fraction of the ET barrier for **1** to be determined by entropy, ranging from 46% for acetonitrile to 69% for chloroform at 25 °C. We do not know why $\Delta S^{\ddagger}$ is observed to be more negative for self-ET reactions of **2** than of **1**, nor why either is as negative as the value observed. The considerations of Figure 1 do not address entropy effects, which are apparently quite important for these ET reactions.

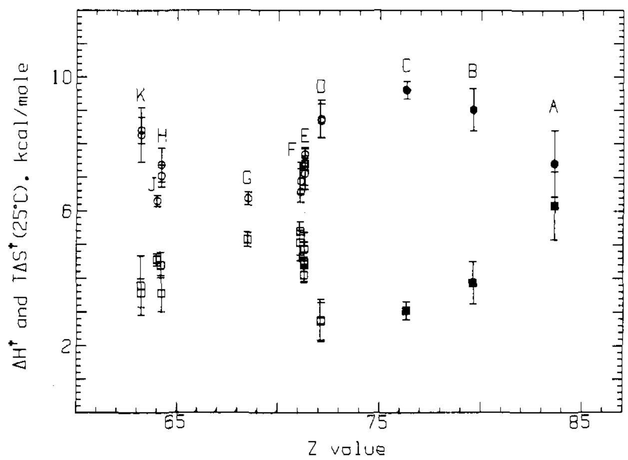


Figure 7. Plot of $\Delta H^{\ddagger}$ (circles) and $T\Delta S^{\ddagger}$ at 25 °C (squares) for $\mathbf{2}/\mathbf{2}^{\bullet+}$ ET as a function of solvent Z value. Error bars represent statistical error in these qualities.

Conclusions

Use of eq 3 and 6 does not give a reasonable value for the distance of the components at the transition state for $\mathbf{2}/\mathbf{2}^{\bullet+}$ ET. The Marcus solvent parameter γ does not quantitatively represent the experimentally measured change of the Marcus λ value for **3** or **4** with solvent. We believe that this point is worth emphasizing, because although Z values are of approximately the same vintage as Marcus theory, use of γ in considering ET solvent effects has been overwhelmingly preferred. The reason for this seems obvious. γ worked far better for the available data. Many compounds for which the Marcus λ value measured from the absorbance maximum, λ_{max}, follows γ very well are available. For example, Creutz's review[17] quotes eight dimeric Ru^{II}, Ru^{III} mixed-value complexes for which solvent effects have been studied in detail, and give straight lines for Marcus λ versus γ plots. We believe it should be noted that these cases have $\lambda_{max}(CH_3CN)$ in the near IR (range 1300–925 nm), Marcus λ 22 to 31 kcal/mol.[18] Self-ET for $\mathbf{1},\mathbf{1}^{\bullet+}$ has a Marcus λ (CH_3CN) value of 19.6 kcal/mol, and ln (k_{et}) for $\mathbf{1},\mathbf{1}^{\bullet+}$ correlates linearly with γ.

In contrast, **3** (CH_3CN: λ_{max} 400 nm, Marcus λ 71.3 kcal/mol) and **4** (CH_3CN: λ_{max} 620 nm, Marcus λ 46.0 kcal/mol) do not show linear dependence of their Marcus λ values with γ, and were used to define the Z and E_T solvent polarity scales, which correlate well with each other.[15d] Self-ET for $\mathbf{2},\mathbf{2}^{\bullet+}$ has a Marcus λ (CH_3CN) value of 47.6 kcal/mol and ln (k_{et}) for $\mathbf{2},\mathbf{2}^{\bullet+}$ correlates well with Z (and E_T). Ionic reactions which follow Z also have substantial barriers.[14,15] We take this as empirically strongly suggestive evidence that different solvent dependence occurs for high- and low-barrier ET processes. We do not doubt that the

---

(17) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

(18) (a) We also note that for Meyer and co-workers' study[18b] of dimeric $(L_3ML'ML_3)^{5+}$ mixed-valence complexes where L_3M = $(bipyridyl)_2ClRu$, the fit of Marcus λ versus γ plots appears to decrease as Marcus λ increases. Discarding the water points (which should not be used anyway), for L′ = pyridazine, $\lambda(CH_3CN)$ = 22.0 kcal/mol, r = 0.998, average deviation of λ = 0.04 kcal/mol; for L′ = 4,4′-bipyridine, λ (CH_3CN) = 29.0, r = 0.979, average deviation of λ = 0.15; L′ = 1,2-(4-pyridyl)ethylene, λ (CH_3CN) = 30.9, r = 0.892, average deviation of λ = 0.50 kcal/mol. Is strict γ dependence the limit at low Marcus λ value? (b) Power, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 1289 and references therein.

Table III. Experimental Data for the Variable-Temperature Data Sets Used in Measuring the Data of Tables I and II

code	solvent	$[\mathbf{2}^{\bullet+}NO_3^-]$[a]	$[\mathbf{2}]/[\mathbf{2}^{\bullet+}]$	T, °C [$\Delta\nu$, Hz] values
A	CD_3OD	11.8	29.1	22.2 [2.16], 0.0 [0.8], 9.9 [1.15], 28.8 [2.95], 39.6 [5.1]
B	C_2D_5OD	9.87	38.5	30.3 [9.4], 40.5 [15.3], 50.3 [25.3], 11.5 [3.35], 21.5 [5.4]
C	C_3D_7-2-OD	6.85	35.7	23.3 [6.5], 10.2 [2.85], 0.2 [1.5], 29.0 [8.85]
D1	CD_3NO_2	6.94	43.4	23.5 [48.0], −19.8 [3.1], −9.6 [6.5], +0.1 [11.85], 10.0 [20.0]
D2	CD_3NO_2	6.22	34.7	23.5 [47.5], −19.0 [3.3], −9.1 [7.2], +0.4 [12.5], 9.7 [21.0]
E1	CD_3CN	5.84	37.8	23.1 [22.6], −19.5 [2.35], −9.5 [4.25], +0.3 [7.15], 10.1 [12.3], 29.0 [29.5]
E2	CD_3CN	4.92	35.1	21.5 [14.2], 9.8 [7.7], −1.9 [4.2], −12.9 [2.4], −19.5 [1.7]
E3	CD_3CN	5.04	25.1	21.7 [19.0], 11.5 [11.0], 0.6 [6.5], −10.5 [3.6]
E4	CD_3CN	5.99	42.1	24.8 [19.5], −18.8 [1.9], −8.8 [3.5], +0.6 [6.2], 10.8 [10.0], 29.6 [24.0]
E5	CD_3CN	5.50	41.6	22.5 [21.6], −18.1 [2.28], −9.2 [4.05], 0.0 [6.7], 9.4 [11.0]
E6	CH_3CN	8.07	35.9	22.2 [28.2], 10.0 [15.5], +0.1 [9.4], −9.4 [6.4], −19.0 [3.6]
F1	$(CD_3)_2SO$	5.99	28.0	22.1 [17.5], 31.8 [25.0], 44.9 [42.0]
F2	$(CD_3)_2SO$	5.34	30.9	23.7 [17.0], 34.2 [26.5], 41.6 [35.0]
G	$(CD_3)_2NCDO$	7.94	24.8	22.9 [51.0], 10.6 [29.6], +0.8 [19.8], −8.4 [12.4], −18.0 [7.7]
H1	CD_2Cl_2	5.04	34.3	22.9 [88.1], 3.5 [32.3], −8.4 [17.1], −22.3 [7.7]
H2	CD_2Cl_2[b]	5.22	40.5	25.7 [42.0], −18.3 [4.6], −8.1 [8.5], +1.6 [14.5], 11.6 [23.0]
J	C_5D_5N	6.18	39.2	22.1 [116.4], 9.4 [67], −0.4 [44.5], −9.9 [27.5], −19.6 [17.0]
K1	$CDCl_3$[c]	9.18	27.4	22.3 [25.65], 9.9 [13.35], +0.1 [7.3], −9.0 [4.0], −19.1 [2.2]
K2	$CDCl_3$[d]	5.59	51.9	24.0 [15.5], −19.5 [1.25], −9.0 [2.2], +2.0 [3.9], 10.3 [7.35], 20.1 [12.5]

[a] Units, mM. [b] For $\mathbf{2}^{\bullet+}\mathbf{OTs}^-$. [c] Contained 0.03% Me_4Si. [d] No Me_4Si.

principal reason that $\mathbf{2}/\mathbf{2}^{\bullet+}$ self-ET has a high barrier is because of its large λ_i value, but the solvent dependence on its ln (k_{et}) is like that of the high Marcus λ unsymmetrical compounds **3** and **4**. λ_i has been assumed to be solvent independent in all treatments we have seen. Obviously it would be desirable to study the solvent dependence for other high Marcus λ value self-ET processes to see if they also follow Z better than γ. We are unable to comment on why the solvent dependence of rate constant appears to be experimentally different for high and low λ_i processes. It should be borne in mind that although the observed self-ET barrier for $\mathbf{2}/\mathbf{2}^{\bullet+}$ has less of an entropy contribution than that of $\mathbf{1},\mathbf{1}^{\bullet+}$, approximately one-third of the observed ET barrier is caused by entropy effects, which we are even less prepared to deal with quantitatively than enthalpy effects.

Experimental Section

Compound Purification. Details of the preparation of **2** and $\mathbf{2}^{\bullet+}NO_3^-$ have already appeared.[19] Neutral **2** was purified by drying ether solutions with anhydrous $MgSO_4$, passing the solution through a pipet packed with neutral alumina, under nitrogen, and crystallization at −20 °C, followed by a second crystallization from dry ether. Traces of solvent were removed from the crystals by five freeze–pump–thaw cycles before use. Samples of $\mathbf{2}^{\bullet+}NO_3^-$ were recrystallized twice from acetonitrile by vapor diffusion. Concentrated solutions in acetonitrile were placed in a larger vial containing ether and allowed to stand under nitrogen at −20 °C overnight. Traces of solvent were removed from the brownish yellow crystals under vacuum.

Solvents. Aldrich CD_3OD, CD_3CD_2OD, i-C_3D_7OD, CD_3NO_2, DMF-d_7, pyridine-d_5, and $CDCl_3$ (without Me_4Si), and Cambridge Isotope Laboratory Me_2SO-d_6, CD_2Cl_2, CD_3CN, and $CDCl_3$ (0.3% Me_4Si) were employed. Fresh ampules were used for each kinetic run. $CDCl_3$ was passed through a microcolumn packed with dry neutral alumina and bulb-to-bulb distilled before use. CD_3CN was passed through a column of dry neutral alumina before use in runs E1 and E2; both high and low values of k_{et} have been seen with and without the alumina treatment.

Typical VT Run (Description of Table III, Run E.1). A solution (500 μL) of 27.7 mg of **2** in 600 μL of deaerated CD_3CN under nitrogen was transferred via syringe to a 5-mm NMR tube filled with N_2 and securely closed with a septum wrapped with Teflon tape. The first FID was collected at ambient temperature (measured by thermocouple), and 50 μL of a solution of 8.1 mg of $\mathbf{2}^{\bullet+}NO_3^-$ in 500 μL of deuterated CD_3CN was added by syringe; a second FID was collected after retuning the instrument. The probe was cooled to low temperature, and 15–30 min was allowed for temperature equilibration. Temperatures were measured by a thermocouple immersed in an NMR tube containing ethanol at each temperature. The instrument was retuned at each temperature. The sample was stored in an ice bath during probe equilibration and temperature measurement. The entire experiment at six temperatures requires about 4 h. NMR data acquisition and treatment have already been published.[8]

Table III contains experimental details for the runs reported in Tables I and II.

Acknowledgment. We thank the National Institutes of Health for partial financial support of this work under Grant GM-29549.

Registry No. 2, 90046-42-7; $\mathbf{2}^{\bullet+}NO_3^-$, 98920-52-6.

---

(19) Nelsen, S. F.; Blackstock, S. C.; Frigo, T. B. *J. Am. Chem. Soc.* **1984**, *106*, 3366.