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Comparison of Intramolecular Electron Transfer Rate Constant with Hush Theory for an Organic Intervalence Compound

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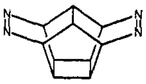
We recently described the conversion of Shen's[1] hexacyclic bis(azo) compound **1** into compounds having identical dinitrogen units that are rather rigidly linked by 4 σ bond shortest pathways and are rather stable in solution in both neutral and cationic oxidation states.[2] One-electron reduction of the bis-*tert*-butylated **1** dication gave bis(hydrazyl) radical cation $\mathbf{2}^{\cdot+}$, and one-electron oxidation of the bis-(*tert*-butylmethylhydrazine) gave bis(hydrazine) radical cation $\mathbf{3}^{\cdot+}$. These species have one dinitrogen unit in the reduced and the other in the oxidized form, making them organic analogues of intervalence transition metal complexes.[3] They show Hush-type charge transfer bands[4] in the near-IR and visible spectral regions, respectively: λ_{max}(CH$_3$CN, 25 °C) = 1199 nm for $\mathbf{2}^{\cdot+}$ and 548 nm for $\mathbf{3}^{\cdot+}$. ESR studies demonstrated that electron transfer (ET) between the dinitrogen units is fast on the ESR time scale for $\mathbf{2}^{\cdot+}$ at −73 °C and slow for $\mathbf{3}^{\cdot+}$ at 87 °C.[2] We report here on the bis(hydrazine) radical cation $\mathbf{4}^{\cdot+}$, in which the "monomeric" dinitrogen unit is the 22/22 sesquibicyclic hydrazine **5**.[5] The latter is isolable in neutral, +1, and +2 oxidation states and has a self-ET rate constant measurable by NMR line broadening.[6] $\mathbf{4}^{\cdot+}$ is the first system for which a Hush analysis of the optical spectrum[3,4] may be directly compared with the rate of thermal electron transfer, providing a significant test of Hush theory.[7]



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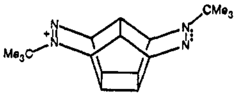

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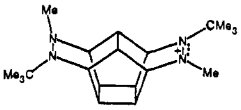

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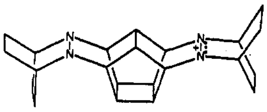

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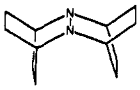

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Although preparation of **5** by the proton-driven Diels–Alder addition of cyclohexadiene to protonated diazabicyclo[2.2.2]octene followed by deprotonation and hydrogenation proceeds in high yield,[5] preparation of **4** proved far more difficult. Formation of the bis(cyclohexadiene) adduct of diprotonated **1** proved very sensitive to conditions (**1**-H$_2^{2+}$ is apparently acidic enough to polymerize cyclohexadiene), and there is little stereoselectivity, so that the diprotonated bis(cyclohexadiene) adduct is a nearly statistical mixture of three compounds, which were not separated. The most serious problems proved to be that retro-Diels–Alder cleavage of the neutral bis(cyclohexadiene) adduct proved faster than hydrogenation, and diimide reduction of the protonated adduct[5d] failed. The discovery by Wang[8] that rhodium on alumina is highly selective for protonated sesquibicyclic hydrazine double bond reduction over N–NH$^+$ and C–NH$^+$ cleavage even in benzylic cases finally allowed preparation of **4** by hydrogenation of the diprotonated **1**–bis(cyclohexadiene) adduct.[9]

First and second electron removal from **4** occur at $E°$ values of −0.45 and −0.27 V vs SCE in CH$_3$CN/0.1 M tetrabutylammonium perchlorate, respectively, allowing preparation of $\mathbf{4}^{\cdot+}$ solutions free from detectable amounts of neutral and dication; coulometric oxidation in acetonitrile or methylene chloride proved convenient for preparation of $\mathbf{4}^{\cdot+}$ from the small amounts of neutral material available. Solutions of $\mathbf{4}^{\cdot+}$ are violet-blue, λ_{max}(CH$_3$CN, 25 °C) = 614 nm, ϵ = 770 M^{-1} cm^{-1}. The absorption band for this nearly saturated species (it formally has one-half of a double bond) can only be plausibly attributed to a Hush-type charge transfer band.[5d]

The ESR spectrum of $\mathbf{4}^{\cdot+}$ in butyronitrile shows the quintet due to coupling to two nitrogen atoms expected for the slow-exchange region[2] at −67 °C and the nonet due to coupling to four nitrogen atoms expected for the fast exchange region[2] at 107 °C.[9] Rate constants obtained by simulation of seven spectra collected from −23 to 77 °C in acetonitrile give a linear Eyring plot[9] from which k_{et}(25 °C) = 1.32(±0.04) × 10^8 s^{-1} was interpolated. Spectral characteristics of the visible band for seven solvents are summarized in Table 1.

According to Marcus theory,[10] the thermal energy barrier to electron transfer is one-quarter of the vertical ET energy gap λ, which for a symmetrical complex showing a Hush CT band like $\mathbf{4}^{\cdot+}$ is equal to the transition energy, E_{op}. λ is the sum of the solvent reorganization energy λ_{out} and the internal reorganization energy λ_{in}, and λ_{out} may be approximated by eq 1. The

$$\lambda_{out} = 332.1(r^{-1} - d^{-1})(\gamma) \tag{1}$$

proportionality constant given produces λ_{out} in kilocalories/mole when the average radius of a monomeric unit, r, and distance between the units' centers, d, are in angstroms. The term γ is a solvent polarity parameter, $\gamma = n^{-2} - \epsilon_s^{-1}$, calculated from the refractive index at the sodium D line, n, and the static dielectric constant ϵ_s. In an alternate treatment also based on a dielectric continuum, λ_{out} is proportional to $\Delta f(x) = f(\epsilon_s) - f(n^2)$, where $f(x) = (x - 1)/(2x + 1)$.[11] Plots of E_{op} vs γ and vs $\Delta f(x)$ are both straight lines for CH$_2$Cl$_2$ and more polar solvents (r = 0.97,

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(1) (a) Shen, K. W. *J. Chem. Soc., Chem. Commun.* **1971**, 391. (b) Shen, K. W. *J. Am. Chem. Soc.* **1971**, *93*, 3064.

(2) Nelsen, S. F.; Chang, H.; Wolff, J. J.; Adamus, J. *J. Am. Chem. Soc.* **1993**, *115*, 12276.

(3) For a review of intervalence complexes, see: Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

(4) (a) Hush, N. S. *Trans. Faraday Soc.* **1961**, 57, 557. (b) Allen, G. C.; Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 357, 391. (c) Hush, N. S. *Coord. Chem. Rev.* **1985**, *64*, 135. (d) Hush, N. S. In *Mixed Valence Compounds*, Brown, D. B., Ed.; Reidel: Dordrecht, Netherlands, 1980; p 151.

(5) (a) Nelsen, S. F.; Blackstock, S. C.; Frigo, T. B. *J. Am. Chem. Soc.* **1984**, *106*, 3366. (b) Nelsen, S. F.; Blackstock, S. C.; Frigo, T. B. *Tetrahedron* **1986**, *42*, 1769. (c) Nelsen, S. F.; Blackstock, S. C.; Haller, K. J. *Tetrahedron* **1986**, *42*, 6101. (d) Nelsen, S. F.; Frigo, T. B.; Kim, Y.; Thompson-Colón, J. A.; Blackstock, S. C. *J. Am. Chem. Soc.* **1986**, *108*, 7926. The monomer radical cation $\mathbf{5}^{\cdot+}$ shows λ_{max}(CH$_3$CN, 25 °C) = 266 nm, ϵ = 1600 M^{-1} cm^{-1}, attributed to its π,π^* transition. (e) Nelsen, S. F.; Frigo, T. B.; Kim, Y. *J. Am. Chem. Soc.* **1989**, *111*, 5387.

(6) (a) Nelsen, S. F.; Blackstock, S. C. *J. Am. Chem. Soc.* **1985**, *107*, 7189. (b) Nelsen, S. F.; Blackstock, S. C.; Kim, Y. *J. Am. Chem. Soc.* **1987**, *109*, 677. (c) Nelsen, S. F.; Wang, Y. Submitted for publication.

(7) A previous study on a bis(hydroxy)urea radical cation (Nelsen, S. F.; Thompson-Colón, J. A; Kaftory, M. *J. Am. Chem. Soc.* **1989**, *111*, 2089) allowed such a comparison at very different temperatures. This system provided far from a reasonable test of Hush theory because of an anomalous optical absorption spectrum, stability problems, and ill-defined and very different geometry for the radical cation and neutral forms.

(8) Nelsen, S. F.; Wang, Y.; Powell, D. R.; Hayashi, R. K. *J. Am. Chem. Soc.* **1993**, *115*, 5246.

(9) See supplementary material.

(10) (a) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265–322. (b) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441. (c) Marcus, R. A. *Discuss. Faraday Soc.* **1960**, *29*, 21.

(11) (a) We thank Prof. Jortner for suggesting that we use this treatment, from a preprint of ref 11b, eq 12. (b) Cortes, J.; Heitele, H.; Jortner, J. Submitted for publication.

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Table 1. Hush Analysis of the CT Band of $\mathbf{4}^{\bullet+}$

solvent	λ_{max}, nm	$E_{op} = h\nu_{max} = \lambda$, kK (kcal/mol)	λ_{out}, kcal/mol	$\nu_{1/2}$, kK	ϵ_{max}, $M^{-1}\,cm^{-1}$	V, cm^{-1} (kcal/mol)
CH_3CN	614	16.2_9 (46.6)	9.0	8.2_1	770	1360 (3.9)
CH_3NO_2	618	16.1_8 (46.3)	8.7	8.1_9	835	1400 (4.0)
$CH_3(CH_2)_2CN$[a]	622	16.0_7 (46.0)	8.4	8.0_7	794	1360 (3.9)
$(CH_3)_2NCHO$	628	15.9_2 (45.5)	8.0	7.5_4	850	1430 (4.1)
$(CH_3)_2SO$	628	15.9_2 (45.5)	8.0	8.5_0	880	1500 (4.3)
CH_2Cl_2	650	15.3_8 (44.0)	6.4	7.9_8	900	1400 (4.0)
$CHCl_3$	630	15.8_7 (45.4)	7.8	8.0_5	810	1360 (3.9)

[a] Corrected for 5% contamination with dication by subtraction of the dication spectrum.

average E_{op} residual 0.15 kcal/mol, and $r = 0.99$, average E_{op} residual 0.10 kcal/mol respectively) and extrapolate to 37.6 kcal/mol at zero solvent polarity parameter, where λ_{out} disappears and $E_{op} = \lambda_{in}$. Values of λ_{out} calculated using $\lambda_{in} = 37.6$ kcal/mol are shown in Table 1. The $\lambda_{out}(CH_3CN)$ of 9 kcal/mol for $\mathbf{4}^{\bullet+}$ when used with the AM1-calculated N–N′ distance of 4.91 Å as d in eq 1 produces an effective r value of 3.92 Å, in excellent agreement with the r value of 3.95 Å calculated from the X-ray structure of "monomer" **5**.[5c] This suggests that λ_{in} for $\mathbf{4}^{\bullet+}$ has been estimated reasonably accurately despite the long extrapolation involved. The least polar solvent, chloroform, shows a higher λ_{out} value than the solvent polarity regressions predict by 3.4 and 3.1 kcal/mol, respectively. We attribute this deviation to an ion-pairing effect; such effects should always be observed in solvents of low enough polarity. A similar anomaly for intermolecular self-ET rate constant k_{ex} has been observed for both sesquibicyclic hydrazines which have been studied in chloroform.[6] Plots of $\ln(k_{ex})$ vs γ are close to linear in the polarity range between acetonitrile and methylene chloride, but k_{ex} in chloroform is smaller than predicted by this line, consistent with λ_{out} being larger than predicted by its polarity. These observations provide welcome confirmation that the intermolecular ET of monomeric hydrazines and the intermolecular ET of bis(hydrazines) are indeed comparable. If methylene chloride also exhibits a smaller ion-pairing effect, λ_{out} estimated from the solvent polarity plot would be too small; if $\lambda_{out}(CH_3CN)$ were really 11 kcal/mol, it would result in an effective r estimate using eq 1 of 3.75 Å.

The ESR and optical data for $\mathbf{4}^{\bullet+}$ allow testing the predictions of Hush theory. Hush estimates the electronic coupling matrix element V (which is half the energy separation of the ground- and excited-state energy surfaces at the ET transition state) using eq 2,[4] which produces a V of about 1400 cm⁻¹ (4.0 kcal/mol) for $\mathbf{4}^{\bullet+}$ (Table 1). The barrier-crossing frequency $h\nu_{in}$ has often been

$$V\,[\mathrm{cm}^{-1}] = (2.06 \times 10^{-2}/d)(h\nu_{max}\nu_{1/2}\epsilon)^{1/2} \qquad (2)$$

accounted for in interpreting experimental rate data using a single effective frequency approximation.[12] Values for $h\nu_{in}$ of 1500 cm⁻¹ or higher have usually been employed for aromatic compounds,[12a,b] but sesquibicyclic hydrazines have many low-frequency pyramidalization modes contributing significantly to the ET barrier, and a significantly lower value of $h\nu_{in}$ should be more appropriate for $\mathbf{4}^{\bullet+}$.[12c] The width at half-height of the $\mathbf{4}^{\bullet+}$ CT band, $\nu_{1/2} = 8200$ cm⁻¹ in CH_3CN, is smaller than predicted. Hush employs eq 3 for $\nu_{1/2}$,[13a] which only fits $\nu_{1/2}$ of $\mathbf{4}^{\bullet+}$ if its $h\nu_{in}$ is 700 cm⁻¹. Using a Hush formula which includes nuclear tunneling to

$$\nu_{1/2} = [F\coth(F)]^{1/2}[16\ln(2)k_BTh\nu_{max}]^{1/2} \qquad (3)$$

calculate k_{et},[13b] the observed rate constant requires $h\nu_{in}$ of about 1295 cm⁻¹, which is quite poor agreement. Simple Hush theory using a single effective frequency approximation does not give the experimental CT bandwidth correctly, and it does not seem likely that the V value estimated using eq 2 is accurate. Equation 2 will produce values of V which are too high if CT band intensity has contributions from other sources, such as coupling to localized electronic excitations.[14] The consistency between the V obtained for $\mathbf{4}^{\bullet+}$ with the 3.3–3.9 range for V of six other saturated bis(hydrazyls) and bis(hydrazines) connected by 4 σ bond shortest pathways in similar geometry,[2] which have $\lambda_{max}(CH_3CN)$ varying from 512 to 1199 nm, show that the constancy of $h\nu_{max}\nu_{1/2}\,\epsilon$ predicted by eq 2 occurs over a wide transition energy range, which suggests to us that coupling with localized electronic states in these saturated compounds is not a major problem. Somewhat smaller V values are consistent with the observed k_{et} using the Golden Rule equation.[9] It seems likely that the bandwidth problem arises from more than one $h\nu_{in}$ frequency being coupled to the electron transfer. Winkler and co-workers[15] have suggested that eq 4,

$$\nu_{1/2} = [8\ln(2)(2k_BT\lambda_{out} + \lambda_{in}h\nu_{in}\coth(h\nu_{in}/2k_BT))]^{1/2} \qquad (4)$$

which separates λ_{out} from λ_{in} effects and can employ more than one inner sphere frequency, is appropriate; the bandwidth can clearly be fitted using low-frequency pyramidalization modes and higher frequency bond stretching modes, both of which should contribute to λ_{in}. It is still not clear to us how to implement tunneling corrections accurately for multiple modes. Work is in progress to make analogues of $\mathbf{2}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$ with the centers fixed at different distances to establish how the rate constant actually changes, and, in collaboration with Timothy Clark, to attempt to more accurately estimate V and the contributions of various $h\nu_{in}$ modes to λ_{in} and for $\mathbf{4}^{\bullet+}$ and other compounds using computations.

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Supplementary Material Available: Preparation of **4**, its ¹H-NMR spectrum, discussion of V from the Golden Rule equation, optical spectrum of $\mathbf{4}^{\bullet+}$ in CH_3CN and CH_2Cl_2, ESR spectrum at –67 and 107 °C in butyronitrile, observed and experimental spectra at –23 and 77 °C in acetonitrile, Eyring plot of the acetonitrile k_{ex} values, and plot of E_{op} vs $\Delta f(x)$ (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(12) (a) Closs and Miller used an $h\nu_{in}$ of 1500 cm⁻¹ for their steroid-linked quinone, biphenyl ET systems; for a review, see: Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440. (b) Grampp and Jaenicke used an $h\nu_{in}$ of 1668 cm⁻¹ for tetramethyl-*p*-phenylenediamine self-ET; see, for example: Grampp, G.; Jaenicke, W. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *95*, 904. (c) Nelsen suggested that $h\nu_{in}$ in a single effective frequency approximation might be as low as 1000 cm⁻¹ for **5** self-ET from consideration of AM1-calculated frequencies; see: Phelps, D. K.; Ramm, M. T.; Wang, Y.; Nelsen, S. F.; Weaver, M. J. *J. Phys. Chem.* **1993**, *97*, 181.

(13) (a) $F = h\nu_{in}/4RT$. (b) From ref 4c, $k_{et} = \kappa_{el}ch\nu_{in}(\lambda_{in}/\lambda)^{1/2}\Gamma_n\exp(-\lambda/4RT)$, where $\Gamma_n = 2F\,\mathrm{csch}(2F)\exp[(-\lambda_{in}/h\nu_{in})(\tanh(F) - F)]$. $\kappa_{el} = 1.00$ for V of 3.9 kcal/mol; the ET is adiabatic if this V is correct. The preexponential factor is 4.6×10^{16} s⁻¹ (which includes a factor of 1350 for Γ_n).

(14) Murrel, J. N. *J. Am. Chem. Soc.* **1959**, *81*, 5037.

(15) Winkler, J. R.; Netzel, T. L.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1987**, *109*, 2381, footnote 35.