vinyl epoxide **1b** with a cinnamyl substituent afforded exclusively the 5-exo product **4b** whereas **1a** afforded a mixture of **4a**, **5a**,[9] and **6a**[10] in a ratio of 12:50:24.[11] The exclusive 6-endo cyclization was realized with **1c** bearing β-methyl substituent[9] and **4c** was not detected. Although the present results are somewhat in contrast with previously reported strong preference for 5-exo cyclization of allylic radicals,[12] it is also well-known that cyclization of stabilized radicals is reversible, allowing thermodynamically favored 6-endo products to compete or even dominate.[13] Furthermore, the control of radical sites in cyclization by introducing a suitable substituent makes the present method versatile and attractive, as seen in **7**.[14]

The radical allylation of allylic halides and related precursors by allylstannanes has not been thoroughly studied.[15,16] Initial attempts with allyltri-*n*-butylstannane and methallyltri-*n*-butylstannane under the standard conditions (0.5 M toluene solution of allylstannane (2.0 equiv) and AIBN (0.1 equiv) at 80 °C for 2 h, method B) failed and starting vinyl epoxides were recovered unchanged. However, it has been found that allylation reactions proceeded smoothly with activated allylstannanes such as 2-carbethoxyallyltri-*n*-butylstannane[15b] and 2-cyanoallyltri-*n*-butylstannane.[17] Thus, treatment of **9** with activated allylstannanes afforded **10a** and **10b**.

The radical reaction of the vinyl endo epoxide **13** was similarly initiated by *n*-Bu₃Sn radical addition, followed by epoxide fragmentation to the alkoxy radical, 1,5-H transfer to produce the carbon centered radical, cyclization,[18] and termination via ejection of *n*-Bu₃Sn radical to afford the cis-fused bicyclic compound as shown in Scheme II.[19,20] The addition of a 0.05 M benzene solution of *n*-Bu₃SnH (0.3 equiv) and AIBN (0.05 equiv) by a syringe pump for 3 h to a 0.05 M refluxing benzene solution of **13a**[21] and an additional stirring for 1 h (method C) afforded **14a** in 60% yield as a 3:2 mixture of diastereomers. The use of the substrate bearing a radical stabilizing group on the side chain improved the yield.[22] The cyclopentenone-derived vinyl epoxide

15[23] led to **16** in lower yield, as compared with **13**.

In conclusion, radical reactions of vinyl epoxides with *n*-Bu₃SnH proceed via radical translocations by a novel 1,5-*n*-Bu₃Sn group or a 1,5-hydrogen atom transfer, provide access to allylic or other carbon centered radicals for use in cyclization or addition reaction, and are highly useful for the synthesis of a variety of carbocyclic compounds.

Supplementary Material Available: Spectral data (¹H NMR, ¹³C NMR, IR, and HRMS) for vinyl epoxides and products (7 pages). Ordering information is given on any current masthead page.

(22) The only detectable byproduct was an enone (<5%), resulting from β-cleavage of the tertiary alkoxy radical.

(23) **15** was prepared from 2-bromo-2-cyclopenten-1-one in four steps (RMgBr, CuBr, Me₂S, TMSCl/LiCl, DMF/H₂O₂-NaOH/Wittig reaction).

(24) **1a**, 70:30; **1b**, 55:45; **1c**, 65:35; **4a**, 65:35; **4b**, 75:25; **5c**, 80:20; **7**, 75:25; **8**, 67:33; **14a**, 60:40; **14b**, 60:40; **14c**, 75:25; **14d**, 50:50; **16a**, 52:48; **16b**, 50:50. The ratio of **1a**, **1b**, **4a**, and **4b** was determined by HPLC and the ratio of the others was determined by ¹H NMR.

Symmetry Effects in Photoinduced Electron Transfer Reactions

Yang Zeng and Matthew B. Zimmt*

Department of Chemistry, Brown University
Providence, Rhode Island 02912

Received March 25, 1991
Revised Manuscript Received May 3, 1991

Electronic symmetry rules have been established for many types of chemical reactions.[1a] The existence of symmetry rules for electron-transfer reactions is of fundamental[1b,c] and practical interest, in view of efforts to develop strategies for the generation of long-lived charge-transfer states.[2] Experimental[3-6] and the-

(7) Recent reviews: Ramaiah, M. *Tetrahedron* **1987**, *43*, 3541. Curran, D. P. *Synthesis* **1988**, 417, 489.

(8) For cyclization of allyl radicals, see: Schwartz, C. E.; Curran, D. P. *J. Am. Chem. Soc.* **1990**, *112*, 9272 and references cited therein.

(9) The structures of **5a** and **5c** were determined by unambiguous synthesis.

(10) For the sake of convenience, the regioisomeric product (the homoallylic alcohol from quenching the tertiary allylic radical by H) is not drawn in Scheme I and its benzoate was inseparable from the benzoate of **6a**. ¹H NMR analysis indicated the presence of a 3:1 mixture of **6a** and the regioisomer.

(11) A mixture of crude products was converted into the corresponding benzoates and the benzoates were separated with HPLC.

(12) Stork, G.; Reynolds, M. E. *J. Am. Chem. Soc.* **1988**, *110*, 6911.

(13) Curran, D. P.; Chang, C.-T. *J. Org. Chem.* **1989**, *54*, 3140. Laird, E. R.; Jorgensen, W. L. *J. Org. Chem.* **1990**, *55*, 9 and references cited therein.

(14) **7** was prepared from *N*-(cyclopentylidene)cyclohexylamine in four steps (LDA, BrCH₂CH₂CH=CHPh/LDA, HCHO/MsCl-pyridine, DBU/Me₂S⁺CH₂⁻.

(15) (a) Keck, G. E.; Enholm, E. J.; Yates, J. B.; Wiley, M. R. *Tetrahedron* **1985**, *41*, 4079. (b) Baldwin, J. E.; Adlington, R. M.; Birch, D. J.; Crawford, J. A.; Sweeney, J. B. *J. Chem. Soc., Chem. Commun.* **1986**, 1339. (c) Lee, E.; Yu, S.-G.; Hur, C.-U.; Yang, S.-M. *Tetrahedron Lett.* **1988**, *29*, 6969.

(16) Only one example of allylation of allyl bromide with allyltri-*n*-butylstannane under UV was reported (Grignon, J.; Servens, C.; Pereyre, M. *J. Organomet. Chem.* **1975**, *96*, 225). However, reaction of 1-bromo-2-nonene with allyltri-*n*-butylstannane under standard Keck conditions did not occur.

(17) 2-Cyanoallyltri-*n*-butylstannane was prepared from 3-hydroxy-2-methylenepropanesulfonylbenzene (Breuilles, P.; Uguen, D. *Tetrahedron Lett.* **1987**, *28*, 6053) in four steps (Swern/NH₂OH-HCl-pyridine/(CF₃CO)₂O, Et₃N/*n*-Bu₃SnH, AIBN).

(18) It may be appropriate to mention that Rawal et al. reported the similar approach based on 1,5-H transfer and cyclization process during our investigation. Rawal, V. H.; Newton, R. C.; Krishnamurthy, V. *J. Org. Chem.* **1990**, *55*, 5181.

(19) Keck, G. E.; Enholm, E. J. *Tetrahedron Lett.* **1985**, *26*, 3311. Danishefsky, S. J.; Panek, J. S. *J. Am. Chem. Soc.* **1987**, *109*, 917.

(20) The stereochemistry of the ring junction is expected to be cis due to geometrical and stereoelectronic reasons. Stork, G.; Mook, R.; Biller, S. A.; Rychnovsky, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 3741. Beckwith, A. L. J.; Roberts, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 5893 and ref 18.

(21) **13** was prepared from 2-cyclohexen-1-one in four steps (RLi/PCC/H₂O₂-NaOH/Wittig reaction).

(1) (a) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1970. (b) Glauser, W. A.; Raber, D. J.; Stevens, B. *J. Phys. Chem.* **1991**, *95*, 1976. (c) Stevens, B. *Chem. Phys.* **1988**, *122*, 347.

(2) (a) Gust, D.; Moore, T. *Science* **1989**, *244*, 35. (b) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 5562.

(3) (a) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047. (b) Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440. (c) Closs, G. L.; Calcaterra, L. T.; Green, N. J.; Penfield, K.; Miller, J. R. *J. Phys. Chem.* **1986**, *90*, 3673. (d) Liang, N.; Miller, J. R.; Closs, G. L. *J. Am. Chem. Soc.* **1989**, *111*, 8740. (e) Closs, G. L.; Johnson, M. D.; Miller, J. R.; Piotrowiak, P. *J. Am. Chem. Soc.* **1989**, *111*, 3751. (f) Ohta, K.; Closs, G. L.; Morokuma, K.; Green, N. J. *J. Am. Chem. Soc.* **1986**, *108*, 1319.

(4) (a) Oevering, H.; Paddon-Row, M. N.; Heppener, M.; Oliver, A. M.; Cotsaris, E.; Verhoeven, J. W.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 3258. (b) Oevering, H.; Verhoeven, J. W.; Paddon-Row, M. N.; Warman, J. M. *Tetrahedron* **1989**, *45*, 4751. (c) Paddon-Row, M. N.; Oliver, A. M.; Warman, J. M.; Smit, K. J.; de Haas, M. P.; Oevering, H.; Verhoeven, J. W. *J. Phys. Chem.* **1988**, *92*, 6958. (d) Pasman, P.; Rob, F.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1982**, *104*, 5127. (e) Verhoeven, J. W. *Pure Appl. Chem.* **1990**, *62*, 1585. (f) Lawson, J. M.; Craig, D. C.; Paddon-Row, M. N.; Kroon, J.; Verhoeven, J. W. *Chem. Phys. Lett.* **1989**, *164*, 120. (g) Warman, J. M.; Smit, K. J.; de Haas, M. P.; Jonker, S. A.; Paddon-Row, M. N.; Oliver, A. M.; Kroon, J.; Oevering, H.; Verhoeven, J. W. *J. Phys. Chem.* **1991**, *95*, 1979. (h) Oliver, A. M.; Craig, D. C.; Paddon-Row, M. N.; Kroon, J.; Verhoeven, J. W. *Chem. Phys. Lett.* **1988**, *150*, 366.

(5) (a) Isied, S. S.; Vassilian, A.; Wishart, J. F.; Creutz, C.; Schwarz, H. A.; Sutin, N. *J. Am. Chem. Soc.* **1988**, *110*, 635. (b) Isied, S. S.; Vassilian, A. *J. Am. Chem. Soc.* **1984**, *106*, 1732. (c) Mayo, S. L.; Ellis, W. R., Jr.; Crutchley, R. J.; Gray, H. B. *Science* **1986**, *233*, 948. (d) Schanze, K. S.; Cabana, L. A. *J. Phys. Chem.* **1990**, *94*, 2740.

(6) (a) Stein, C. A.; Lewis, N. A.; Seitz, G. *J. Am. Chem. Soc.* **1982**, *104*, 2596. (b) Leland, B. A.; Joran, A. D.; Felker, P. M.; Hopfield, J. J.; Zewail, A. H.; Dervan, P. B. *J. Phys. Chem.* **1985**, *89*, 5571.

Table I

| solvent [E_{00},[a] eV]	$1/\tau(4)$,[c] 10^7 s^{-1}	$\Delta G°(1)$,[d] eV	$k_{ET}(1)$,[e] 10^7 s^{-1}	$\Delta G°(2)$,[d] eV	$k_{ET}(2)$,[e] 10^7 s^{-1}	$\Delta G°(3)$,[d] eV	$k_{ET}(3)$,[e] 10^7 s^{-1}	$|V|(1)$,[f] cm^{-1}	$|V|(2)$,[f] cm^{-1}	$|V|(3)$,[f] cm^{-1}
Et$_2$O [3.09]	3.70	−0.30	2.0	0.04	1.4	−0.07	18.8	1.3	23	13
EA[b] [3.05]	3.12	−0.38	4.8	−0.05	16.5	−0.13	44.1	1.9	53	17
THF [3.04]	3.38	−0.42	5.1	−0.10	33.6	−0.17	57.2	1.7	50	15
ACN[b] [3.00]	2.43	−0.59	2.5	−0.29	7.1	−0.31	9.8	1.6	26	8.3
PC[b] [2.97]	2.70	−0.59	5.7	−0.29	17.2	−0.30	23.3	1.9	27	9.8

[a] E_{00} evaluated as the energy at the intersection of the scaled S$_1$ absorption and fluorescence spectra. [b] EA, ethyl acetate; ACN, acetonitrile; PC, propylene carbonate. [c] Standard deviation of lifetime measurements $<\pm10\%$. [d] Exothermicities calculated as in ref 4a. [e] Standard deviation of electron-transfer (ET) rate constants $<\pm20\%$. [f] Parameters in the semiclassical calculation: $\lambda_v = 0.35$ eV, $h\nu = 1400$ cm^{-1}, $T = 295$ K; $R_{cc}(1) = 11.9$ Å, $R_{cc}(2) = 12.1$ Å, $R_{cc}(3) = 8.6$ Å.

oretical[7-9] studies have established that electron-transfer rate constants in donor–spacer–acceptor (DSA) molecules are determined, in part, by the DSA structure. Numerous DSA systems exhibit a monotonic decrease in transfer rate constant with an increase in the number of bonds comprising the shortest path between the donor and acceptor.[3-6] However, stereoelectronic effects on transfer rate constants have been systematically studied in only a few systems. Of particular importance are (1) the dependence on donor and acceptor attachment geometry with respect to the spacer as demonstrated by Closs and Miller,[3] (2) the large dependence on the dihedral angle between donor and acceptor in linked diporphyrin molecules found by McLendon,[10] (3) the small dependence on donor/acceptor dihedral angle reported by Sakata,[11] and (4) the significant decrease effected by substitution of gauche for trans links in the spacer[4] originally predicted by Hoffmann.[12] We have initiated studies aimed at identifying novel DSA structural features which modulate electron-transfer rate constants. Herein, we report results that demonstrate the existence of electronic symmetry effects on photoinduced electron transfer rate constants.

The golden rule expression for the electron transfer rate constant is commonly reduced[3,7,8,13] to the product of a Franck–Condon weighted density of states (FCWDS) and an electronic coupling matrix element squared, $|V|^2$, which is determined by the mixing of the initial and final electronic states. In principle, the magnitude of $|V|$ can be modulated from a maximum to near 0 by varying the relative orientation of the donor and acceptor.[3f,8] Symmetry considerations can be used to devise rigid DSA molecules for which $|V|$ and the electron-transfer rate constant are both formally 0 at the equilibrium geometry. However, vibrations and vibronic interactions will relax the symmetry constraint, resulting in a nonzero $|V|$. The magnitude of the residual, symmetry-induced rate restriction must, therefore, be experimentally determined.[14a]

The rigid polycyclic norbornane structures originally investigated by Paddon–Row[15] and employed in studies of photoinduced electron transfer reactions in collaborations with Verhoeven, Hush, Warman,[4] and Miller[16] provide some of the best structures for

evaluation of symmetry effects on electron transfer. These authors have discussed[14a] the apparent absence of symmetry effects[14b] on electron-transfer rate constants and charge-transfer absorption spectra in DSAs containing dimethoxynaphthalene donors. On the basis of their observations, we chose 1,4-dimethoxyanthracene as the (photoexcited) donor to obtain reduced driving force for electron transfer and in an attempt to initiate electron transfer from a ^1L_a-derived excited (S$_1$) state.[17] Compounds 1–3 exhibit approximate C_s symmetry and rigidly hold the donor and an electron acceptor at a separation of seven σ bonds. Within the C_s point group, the donor S$_1$ state exhibits A″ symmetry, whereas the lowest energy states formed by electron transfer from the donor to the acceptor exhibit A′, A″, and A″ symmetries, in 1–3, respectively. Thus, electron transfer is formally symmetry forbidden in 1 but allowed in 2 and 3. 1 and 2 contain all trans arrangements of the spacer C–C backbone whereas 3 possesses a single gauche link.[18]
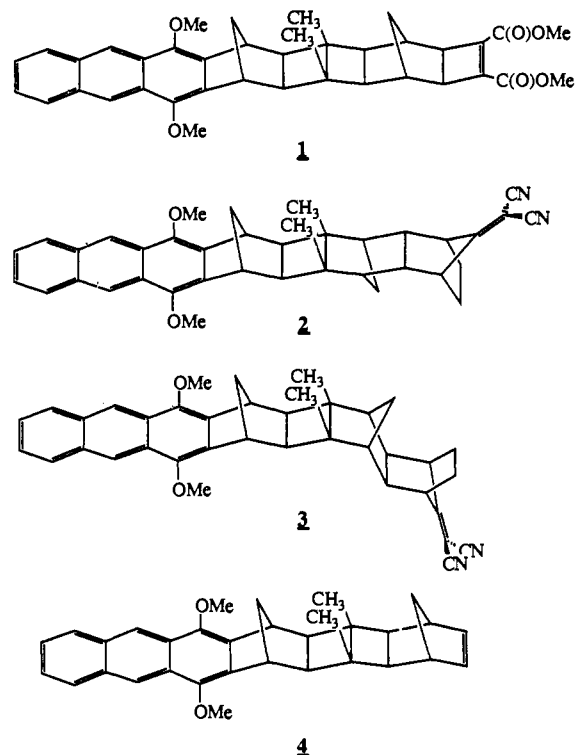
The absorption spectra of 1–3 and a donor-only model compound, 4, are identical from 300 to 400 nm. No evidence of charge-transfer absorption was found in any solvent. In each solvent, the fluorescence spectra of 1–4 are identical except for

(7) (a) Beratan, D. N.; Hopfield, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 1584. (b) Beratan, D. N. *J. Am. Chem. Soc.* **1986**, *108*, 4321. (c) Onuchic, J. N.; Beratan, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 6771.

(8) (a) Siders, P.; Cave, R. J.; Marcus, R. A. *J. Chem. Phys.* **1984**, *81*, 5613. (b) Cave, R. J.; Siders, P.; Marcus, R. A. *J. Phys. Chem.* **1986**, *90*, 1436.

(9) (a) Mikkelsen, K. V.; Ratner, M. A. *Chem. Rev.* **1987**, *87*, 113. (b) Larsson, S. *J. Am. Chem. Soc.* **1981**, *103*, 4034.

(10) (a) Heiler, D.; McLendon, G.; Rogalskyj, P. *J. Am. Chem. Soc.* **1987**, *109*, 604. (b) Seminar: Brown University, 1989.

(11) Sakata, Y.; Nakashima, S.; Goto, Y.; Tatemitsu, H.; Misumi, S.; Asahi, T.; Hagihara, M.; Nishikawa, S.; Okada, T.; Mataga, N. *J. Am. Chem. Soc.* **1989**, *111*, 8979.

(12) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

(13) Kestner, N. R.; Logan, J.; Jortner, J. *J. Phys. Chem.* **1974**, *78*, 2148.

(14) (a) For discussion of symmetry effects on the charge-transfer absorptions and forward versus reverse electron transfer rate constants in the polynorbornane DSA molecules, see refs 4 and 17. (b) We are not aware of a *comparative* study of symmetry effects on excited-state electron-transfer rate constants in the polynorbornane DSA series.

(15) (a) For a summary of synthetic and photoelectron spectroscopic results, see: Paddon-Row, M. N.; Cotsaris, E.; Patney, H. K. *Tetrahedron* **1986**, *42*, 1779. (b) Paddon-Row, M. N. *Acc. Chem. Res.* **1982**, *15*, 245.

(16) Penfield, K. W.; Miller, J. R.; Paddon-Row, M. N.; Cotsaris, E.; Oliver, A. M.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 5061.

(17) (a) Larsson, S.; Volosov, A. *J. Chem. Phys.* **1987**, *87*, 6623. (b) Hush, N. S. In *Supramolecular Photochemistry*; Balzani, V., Reidel, D., Eds.; NATO ASI Series C 214; Reidel: Dordrecht, 1987; p 53. (c) Reimers, J. R.; Hush, N. S. *Chem. Phys. Lett.* **1990**, *169*, 622.

(18) Stereochemical assignments of structures 1–3 and their precursors were derived from 400-MHz ^{1}H NMR decoupling and NOE studies and from an X-ray structure of 2. These results and the syntheses will be reported elsewhere.

the overall intensities, which decrease in the order **4 > 1 > 2 > 3**. Table I lists fluorescence decay rate constants[19a] for **4** and electron-transfer rate constants[19b] and exothermicities[19c] for **1–3** in five solvents.

In solvents more polar than diethyl ether,[25] the electron-transfer rate constants in DSAs **2** and **3** are from three to seven and from four to 11 times larger, respectively, than those in DSA **1**. Hence, either $|V|$ or the FCWDS must be larger in **2** and **3**. Since electron transfer in **1** is 0.3 eV more exothermic (Table I) than in **2** and the center to center distances (R_{cc}) are comparable, $|V|$ in DSA **2** must be larger than in DSA **1**.[20] This qualitative conclusion is supported by the $|V|$'s, listed in Table I, that were obtained[21] from the electron-transfer data using the semiclassical formulation of the transfer rate constant[13] in conjunction with Marcus' expression for the solvent reorganization energy[22] and the Born correction to the reaction exothermicity.[4] DSAs **1** and **2** are nearly linear and contain all trans arrays of spacer bonds; thus, the dominant contribution to $|V|$ is through-bond coupling.[4] $|V|$ in the symmetry-forbidden DSA, **1**, is only 4–7% as large as in the symmetry-allowed DSA, **2**. The reduction in $|V|$ from **2** to **1** translates into a 200–800-fold reduction in the optimal transfer rate constant[23] for the symmetry-forbidden DSA, which represents the symmetry restriction to electron transfer in these molecules.

Qualitative comparison of the transfer rate constants in **3** to those of **1** and **2** is made difficult by the gauche link in the spacer of **3**. The shorter R_{cc} in **3** effects a decrease in the solvent reorganization energy and increases in the driving force and FCWDS in comparison to **2**. Furthermore, through-bond contributions to $|V|$ are likely reduced by the gauche link[4,12] in **3**, whereas through-solvent coupling could be augmented.[4e,24] Neglecting the results from diethyl ether,[25] quantitative analysis (Table I) indicates that introduction of a single gauche link in the symmetry-allowed spacers (**2 → 3**) diminishes the optimal transfer rate constant[23] by a factor of 3–11. This concurs with results of Oliver et al., who have reported[4h] rate reductions by factors of 3–14 attending a single trans to gauche substitution in DSAs with nearly identical R_{cc}'s. We have not yet determined the contribution of through-solvent coupling in **3**. Furthermore, we have not identified the cause of the factor of 2 reduction in $|V|$(**2**) and $|V|$(**3**) observed in the more polar solvents, particularly since $|V|$(**1**) is effectively solvent independent. The larger $|V|$ in THF, ethyl acetate, and ether (**3**) could originate from symmetry-dependent through-solvent coupling. Alternatively, inadequate values of the sol-

vent-dependent reaction and reorganization energies could be responsible.

Within the standard model,[4,13,22] these experiments demonstrate that electronic symmetry *can* modulate electron-transfer rate constants by at least 2 orders of magnitude. This observation is consistent with literature methods for evaluation of electronic coupling matrix elements, which reduce to 0 for appropriate DSA symmetries.[3,8,9] In order to experimentally achieve larger symmetry restrictions, the contributions of vibrations and vibronic coupling to the relaxation of the symmetry constraints must be better understood. If S_1–S_n vibronic coupling contributes significantly to the electronic mixing, $|V|$ could be temperature dependent. Measurement of the temperature dependence of the electron-transfer rate constants and the dependence of the redox potential on solvent and temperature will provide more quantitative characterization of $|V|$. Moreover, elimination of the larger reaction exothermicity and conformational freedom associated with the acceptor in **1** will provide a more direct measure of symmetry effects in electron-transfer reactions. These experiments are currently in progress.

Tethered Oligonucleotide Probes. A Strategy for the Recognition of Structured RNA

Paul L. Richardson and Alanna Schepartz*

*Sterling Chemistry Laboratory, Yale University
225 Prospect Street, New Haven, Connecticut 06511*

Received February 7, 1991

The past decade has been marked by research directed toward the design of compounds capable of recognizing DNA sequences[1,2] and shapes.[3] Molecules capable of recognizing RNAs are virtually unknown,[4] largely because of the structural complexity of these macromolecules[5] and the scarcity of information describing their

---

(19) (a) Fluorescence waveforms obtained with a Hamamatsu R1645U microchannel plate connected to a Tektronix TD7912 digitizer. Lifetimes obtained by nonlinear least squares fitting waveforms to the system response convolved with a single exponential decay. (b) Electron-transfer rate constants determined as $(1/\tau(X)) - (1/\tau(4))$. (c) Redox potentials measured by using cyclic voltammetry at 22 °C in CH_3CN containing 0.1 M tetrabutylammonium hexafluorophosphate versus Ag/AgCl. The oxidation potential of the donor is 0.894 eV. The reduction potentials of the dicarbethoxyethylene and dicyanoethylene acceptors are −1.64 eV and −1.9 eV, respectively. The dicyanoethylene reduction waveform is irreversible at scan rates of 100 mV/s. The reduction potential is accurate to within 100 mV (see ref 4a). The reaction exothermicity was calculated as in ref 4a.

(20) The reaction exothermicities are insufficient to access the inverted region in these solvents.

(21) The matrix element calculation is sensitive to the Born radii assumed for the donor and acceptors. Changing the acceptor radii in the range from 3.0 to 5.0 Å generates $|V(2)|/|V(1)|$ ratios of 3–40 in acetonitrile. The acceptor radii employed are 3.9 and 4.2 Å for the acceptors in **2** and **1**, respectively, and 5.0 Å for the donor. As experimental values for these radii are lacking, the radii were obtained from the equivalent excluded volume spheres. We are attempting to determine these radii from electrochemical measurements.

(22) (a) Marcus, R. A. *Can. J. Chem.* **1959**, *37*, 155. (b) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966.

(23) The optimal transfer rate constant is proportional to $|V|^2$ and refers to the situation where FCWDS is 1.

(24) (a) Miller, J. R.; Beitz, J. V.; Huddleston, R. K. *J. Am. Chem. Soc.* **1984**, *106*, 5057. (b) Miller, J. R.; Peeples, J. A.; Schmitt, M. J.; Closs, G. L. *J. Am. Chem. Soc.* **1982**, *104*, 6488. (c) Miller, J. R.; Beitz, J. V. *J. Chem. Phys.* **1981**, *74*, 6746. (d) Guarr, T.; McGuire, M. E.; McLendon, G. *J. Am. Chem. Soc.* **1985**, *107*, 5104.

(25) In diethyl ether, the nearly thermoneutral transfer in **2** and **3** could produce repopulation of S_1 from the electron-transfer state, an increase in the observed lifetime, and a decreased $|V|$.

*To whom correspondence should be addressed.

(1) Dreyer, G. B.; Dervan, P. B. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 968–972. Chu, C. F.; Orgel, L. E. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 963–967. Dervan, P. B. *Science* **1986**, *232*, 464–471. Chen, C. H. B.; Sigman, D. S. *Science* **1987**, *217*, 1197–1201. Helene, C.; Thuong, N. T. *Nucleic Acids Mol. Biol.* **1988**, *2*, 105–123. Corey, D. R.; Pei, D.; Schultz, P. G. *J. Am. Chem. Soc.* **1989**, *111*, 8523–8525. Pei, D.; Schultz, P. G. *J. Am. Chem. Soc.* **1990**, *112*, 4579–4580. Corey, D. R.; Pei, D.; Schultz, P. G. *Biochemistry* **1990**, *28*, 8277–8286. Moser, H. E.; Dervan, P. B. *Science* **1987**, *238*, 645–650. Griffin, L. C.; Dervan, P. B. *Science* **1989**, *245*, 967–971. Strobel, S. A.; Dervan, P. B. *Science* **1990**, *249*, 73–75. Sun, J.-S., et al. *Proc. Natl. Acad. Sci. U.S.A.* **1989**, *86*, 9198–9202. Francois, J. C.; Saison-Behmoaras, T.; Chassignol, M.; Thuong, N. T.; Helene, C. *J. Biol. Chem.* **1989**, *264*, 5891–5898.

(2) Uhlmann, E.; Peyman, A. *Chem. Rev.* **1990**, *90*, 543–584.

(3) Barton, J. K.; Basile, L. A.; Danishefsky, A.; Alexandrescu, A. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 1961–1965. Barton, J. K. *Science* **1986**, *233*, 727–734. Mei, H. Y.; Barton, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 7414–7416. Pyle, A. M.; Long, E. C.; Barton, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 4520–4523.

(4) Zuckermann, R. N.; Schultz, P. G. *Proc. Natl. Acad. Sci. U.S.A.* **1989**, *86*, 1766–1770. Chow, C. S.; Barton, J. K. *J. Am. Chem. Soc.* **1990**, *112*, 2839–2841. Carter, B. J.; de Vroom, E.; Long, E. C.; van der Marel, G. A.; van Boom, J. H.; Hecht, S. M. *Proc. Natl. Acad. Sci. U.S.A.* **1990**, *87*, 9373–9377.

(5) Wyatt, J. R.; Puglisi, J. D.; Tinoco, I., Jr. *BioEssays* **1989**, *11*, 100–106.