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One-Electron Oxidation of Tetraalkylhydrazines

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Loss or gain of a single electron is one of the most fundamental of molecular transformations.[1] It is not quite a "normal" reaction since a bond is not made or broken, but electrochemists recognize the process as a half-reaction.

The vast majority of organic electron-transfer reactions which have been studied seem, in principle, to be rather simply understood. The thermodynamic ability to gain or lose an electron is determined by the energies of the lowest unoccupied and highest occupied molecular orbitals (LUMO and HOMO, respectively) of the species. Excellent correlations are found between vapor-phase electron affinity, or ionization potential (experimental measure of LUMO or HOMO energy), or calculated LUMO (or HOMO) energy, and solution reduction (or oxidation) potential.[1] Most correctly, the thermodynamically significant formal potential for electron transfer, $E^{\circ\prime}$,[2] a measure of ΔG° for electron transfer relative to that of the reference electrode employed, should be used, but the kinetically affected potentials derived from electrochemically irreversible processes are also found to correlate successfully in many cases.[1,3]

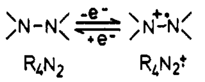
Kinetics for electron transfer in solution are essentially completely determined by the thermodynamics of the reaction considered. When exothermic, electron transfer is so fast that the rate is controlled by the diffusion rates of the reactants. Even when self-exchange (reaction between radical ion and neutral form of the same species), for which ΔG° is zero, is observed, second-order rate constants above about 10^8 M^{-1} s^{-1} are seen for exchanges between aromatic hydrocarbons and their radical anions.[4]

Treatment of the rates for such electron-transfer processes by Marcus theory[5] and its correction for strongly exothermic reactions by Weller and others[6] have been most successful and has led to great advancement of our ability to understand complex reaction schemes where electron transfer is only one of several processes occurring. The kinds of organic systems showing these electron-transfer characteristics are those with large π systems over which the charge (and spin) of the radical ion may be delocalized, allowing sufficient radical ion lifetime so that electron transfer may be studied independently of other processes, and which do not undergo much geometrical change upon electron removal or addition.

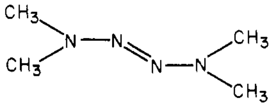
Stephen F. Nelsen was born in Chicago in 1940 and received his B.S. from the University of Michigan and his Ph.D. from Harvard University, working with P. D. Bartlett. He joined the faculty at the University of Wisconsin, where he is now Professor, in 1965.

Tetraalkylhydrazine Radical Cations

In this Account we discuss the single-electron oxidation of tetraalkylhydrazines (R_4N_2) (eq 1). The possibility of studying eq 1 independently of the following reactions which greatly complicate electron-transfer studies of most other saturated amino nitrogen compounds was discovered by accident. Nelsen[7] and Michejda and coworkers[8] found independently that acylation or alkylation of tetramethyl-2-tetrazene gave the ESR spectrum of tetramethylhydrazine radical cation, which was quite persistent. Although it had been long known that dimethylamino-substituted π systems have long-lived radical cations, the earliest and most notable example being Wurster's Blue,[9] the cation



(1)



tetramethyl-2-tetrazene

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(1) For an excellent review of organic electron-transfer reactions, see: Szwarc, M.; Jagur-Grodzinski, J. "Ions and Ion Pairs in Organic Reactions", Szwarc, M., Ed.; Wiley: New York, 1974; pp 1–150.

(2) We employ $E^{\circ\prime}$ to represent experimentally measured formal potentials, in a given solvent, supporting electrolyte system, referenced to a given reference electrode. The work reported here was in acetonitrile containing 0.1 M $NaClO_4$ or tetra-*n*-butylammonium perchlorate, referenced to sce. Slightly different numbers are obtained with the two supporting electrolyte systems, but in all cases checked, the $NaClO_4$ numbers were uniformly 0.05 V lower than the tetra-*n*-butylammonium perchlorate numbers.

(3) Miller, L. L.; Nordblum, G. D.; Mayeda, E. A. *J. Org. Chem.* **1972**, *37*, 916.

(4) Reference 1, p 57 ff.

(5) (a) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 996; (b) **1965**, *43*, 679; (c) *Discuss. Faraday Soc.* **1960**, *29*, 21.

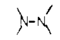
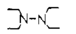
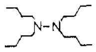
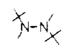
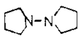
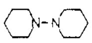
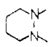
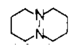
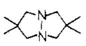
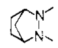
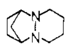
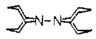
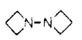
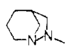
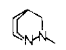
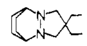
(6) (a) Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 834. (b) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259. (c) Scandola, R.; Balzani, V. *J. Am. Chem. Soc.* **1979**, *101*, 6140.

(7) Nelsen, S. F. *J. Am. Chem. Soc.* **1966**, *88*, 5666.

(8) Brunning, W. H.; Michejda, C. J.; Romans, D. *J. Chem. Soc., Chem. Commun.* **1967**, 11.

0001-4842/81/0114-0131$01.25/0

Table I
PE, Electrochemical, and ESR Data for Selected Tetraalkylhydrazines

compound	IP_1, eV	$IP_2 - IP_1$, eV	est. θ, deg	ΔIP_1,[a] kcal/mol	$\Delta(\Delta G°)$,[b] kcal/mol	a(N), G
 1	8.27	0.55	gauche	[0]	[0]	13.4
 2	7.94	0.51	gauche	−7.6	−0.9	13.0
 3	7.66	0.54	gauche	−14.1	−0.9	
 4	7.67	0.51	gauche	−13.8	+5.5	11.9
 5	7.91	0.56	gauche	−8.3	−7.1	12.9
 6	7.89	0.52	gauche	−8.8	+1.6	
 7ee	7.75	2.26	180	−12.0	−2.3	13.1
7ae	7.75	1.04	~70	−12.0		
 8	7.61	2.31	180	−15.2	−1.2	13.9
 9	7.53	2.21	0	−17.1	−7.8	16.8
 10	7.66	1.78	~120	−14.1	−4.1	16.0
 11	7.19	2.11	<180	−24.9	−9.5	
 12	6.94	2.13	180	−30.7	−7.8	13.2
 13	8.25	0.73	gauche	−0.5	+1.2	14.8
 14	7.63	unobs	0	−14.8	+11.1	26.8
 15	8.18	obs	gauche	−2.1	+9.2	
 16	8.02	0.51	gauche	−5.8	>+12.9	
 17	6.92	2.32	0	−31.1	−12.2	18.5

[a] $\Delta IP_v = IP_1(R_4N_2) - IP_1(Me_4N_2)$. [b] $\Delta(\Delta G°) = 23.06[E°'(R_4N_2) - E°'(Me_4N_2)]$, in acetonitrile, vs. sce.

of tetramethyl-*p*-phenylenediamine, it was a surprise to us that conjugation with a π system is not required for long radical cation lifetime. Other saturated compounds which give long-lived radical cations remain rare.[10–14] In all other known cases, special geometrical features for the alkyl substituents are required for radical cations to be persistent. In contrast, most examples of R_4N_2 have stable enough radical cations to allow measurement of $E°'$ by cyclic voltammetry (CV). These compounds thus provide a unique opportunity to study the effect of changing the weakly interacting alkyl substituents on the stability of the cation radical and also to provide examples for consideration of how controllable geometry changes affect the stability of a two-center, three-electron system, the prototype for many odd-electron species (olefin and ketone radical anions, nitroxyl radicals).

A great contrast between the thermodynamics for electron loss for tetraalkylhydrazines (those from Table I) and for polycondensed aromatic hydrocarbons is illustrated by the plot of $E°'$ vs. first vertical ionization potential (IP) shown as Figure 1. The hydrocarbons fall on a good straight line with a slope of 0.9, but virtually no correlation is found for the hydrazines, all of which fall well below the hydrocarbon line. The tetraalkylhydrazines are thermodynamically much easier to oxidize in solution than hydrocarbons of the same ionization potential. The rest of this Account is devoted to understanding why those classes of compounds behave so differently and the implications of the great thermodynamic differences for electron-transfer kinetics.

Energetics of Single Electron Removal of R_4N_2

Postulated Influence of Lone-Pair/Lone-Pair Dihedral Angle on the Ease of Oxidation. Our in-

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(9) Forrester, A. R.; Hay, J. M.; Thomson, H. R. "Stable Free Radicals"; Academic Press: New York, 1968; pp 254–261.

(10) Examples include the σ-conjugated Dabco cation[11] and an increasing number of three-electron σ-bonded cations in NN,[12] SS,[13] and NS[14] systems.

(11) McKinney, T. M.; Geske, D. H. *J. Am. Chem. Soc.* **1965**, *87*, 3013.

(12) (a) Alder, R. W.; Sessions, R. B.; Mellor, J. M.; Rawlins, M. F. *J. Chem. Soc., Chem. Commun.* **1977**, 747. (b) Alder, R. W.; Sessions, R. B. *J. Am. Chem. Soc.* **1979**, *101*, 3651. (c) Nelsen, S. F.; Haselbach, E.; Gschwind, R.; Klemm, U.; Lanyova, S. *Ibid.* **1978**, *100*, 4367.

(13) (a) Musker, W. K.; Wolford, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3055. (b) Musker, W. K.; Wolford, T. L.; Roush, P. B. *Ibid.* **1978**, *100*, 6416. (c) Wilson, G. S.; Swanson, D. D.; Klug, J. T.; Glass, R. S.; Ryan, M. D.; Musker, W. K. *Ibid.* **1979**, *101*, 1040.

(14) Musker, W. K.; Hirschon, A. S.; Doi, J. T. *J. Am. Chem. Soc.* **1978**, *100*, 7754.

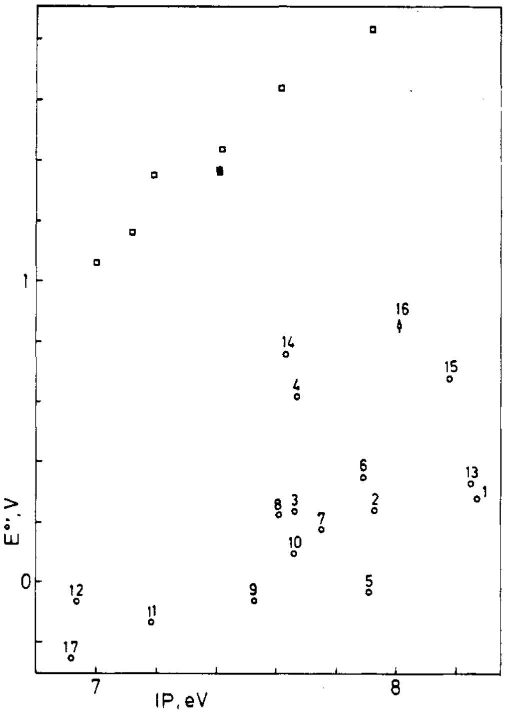

Figure 1. Plot of $E^{\circ\prime}$ (CH_3CN vs. sce) vs. first vertical ionization potential, IP. The squares are for fused aromatic compounds, and the circles are the R_4N_2 entries of Table I.

itial idea in studying eq 1 was that the lone-pair/lone-pair dihedral angle θ (see I) would be the crucial

I

factor in determining the ease of electron removal from hydrazines. The HOMO of a hydrazine is one of the lone-pair combination molecular orbitals which are dominated by the symmetric and antisymmetric combinations of the two lone-pair atomic orbitals (AOs) and which we will call n_+ and n_-. The degree of overlap and hence the n_+,n_- energy separation ought to be strongly dependent upon θ, as suggested in Figure 2, in which the calculated energy of two sp^3 hybrids held at the NN distance in hydrazine is plotted against θ.[15] Because both orbitals are filled, our thoughts ran, the HOMO would be especially destabilized near $\theta = 0$ and 180° where the n_+,n_- energy gap is large, making electron removal easy.

This qualitative prediction proves to be largely incorrect, for illuminating reasons. Understanding Figure 1 requires knowing both how the vapor-phase ionization potential (the horizontal axis) and how the solution-phase standard potential (the vertical axis) of hydrazines are affected as the alkyl groups are changed. Separate types of experiments are of course used in measuring these numbers, and the experiments are discussed separately below.

Vapor-Phase Electron Removal: The Photoelectron Spectra of Hydrazines. The most direct experimental technique for determination of electronic energy levels is photoelectron spectroscopy,[16] and the

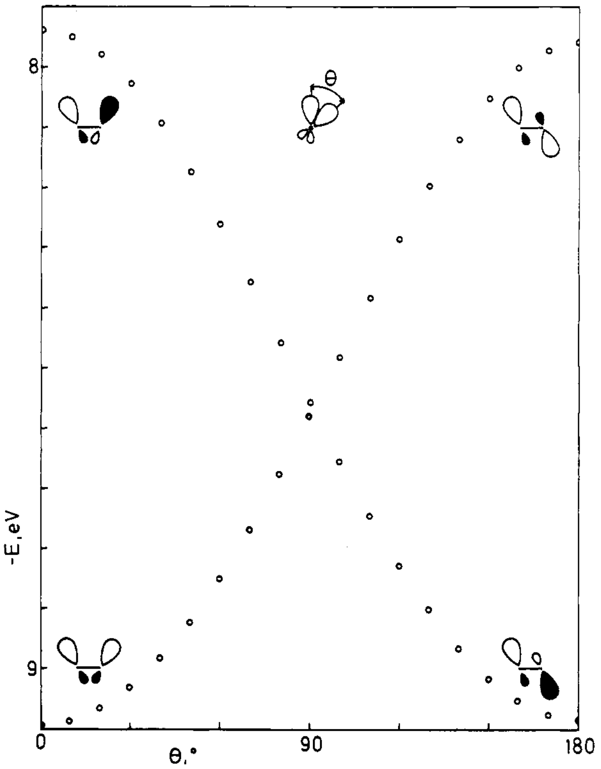

Figure 2. Energies for two sp^3 orbitals held at a distance of 1.45 Å as a function of rotational angle θ. Redrawn from the Ph.D. Thesis of J. M. Buschek, University of Wisconsin—Madison, 1973.

PE spectra of many hydrazines[17-21] bear out the strong n_+,n_- energy gap dependence upon θ predicted in Figure 2, with a couple of significant corrections. When a molecule undergoes a large enough structural change upon electron loss, and hydrazines do, vibrational structure is completely lost in the PE band observed. The PE time scale is exceedingly short (it approximates the time for light to travel molecular distances), so the initial ionization product is the radical cation with a geometry close to that of the neutral molecule. When this geometry is very far from that of the equilibrium radical cation, the radical cation is formed far up in its energy well, where it has essentially a continuum of states. Under these circumstances, the vertical ionization potential (IP_v, the energy gap between R_4N_2 and $R4N_2^{+\cdot}$ in the same geometry as the neutral species) is easily determined—it is the maximum of the broad observed PE band, which is experimentally Gaussian in shape. The adiabatic ionization potential (IP_{ad}, the energy gap between R_4N_2 and $R_4N_2^{+\cdot}$ in its equilibrium

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[15] For details of the calculation, see the Ph.D. Thesis of J. M. Buschek, University of Wisconsin—Madison, 1973.

[16] (a) Turner, D. W. "Molecular Photoelectron Spectroscopy"; Wiley-Interscience: New York, 1970. (b) Eland, J. D. H. "Photoelectron Spectroscopy"; Wiley: New York, 1974. (c) Rabalais, J. W. "Principles of Ultraviolet Photoelectron Spectroscopy"; Wiley-Interscience: New York, 1976.

[17] (a) Rademacher, P. *Angew. Chem.* **1973**, *85*, 410. (b) Rademacher, P. *Tetrahedron Lett.* **1974**, 83. (c) Rademacher, P. *Chem. Ber.* **1975**, *108*, 1548. Rademacher, P.; Koppman, H. *Ibid.* **1975**, *108*, 1557.

[18] (a) Nelsen, S. F.; Buschek, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 2011. (b) Nelsen, S. F.; Buschek, J. M.; Hintz, P. J. *Ibid.* **1973**, *95*, 2013. (c) Nelsen, S. F.; Buschek, J. M. *Ibid.* **1975**, *96*, 2392. (d) Nelsen, S. F.; Buschek, J. M. *Ibid.* **1974**, *96*, 6982. (e) Nelsen, S. F.; Buschek, J. M. *Ibid.* **1976**, *98*, 987.

[19] (a) Nelsen, S. F.; Peacock, V.; Weisman, G. R. *Ibid.* **1976**, *98*, 5269. (b) Nelsen, S. F.; Peacock, V. E.; Weisman, G. R.; Landis, M. E.; Spencer, J. A. *Ibid.* **1978**, *100*, 2806. (c) Nelsen, S. F.; Peacock, V. E.; Kessel, C. R. *Ibid.* **1978**, *100*, 7017. (d) Nelsen, S. F. *Israel J. Chem.* **1979**, *18*, 45.

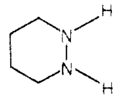
[20] Nelsen, S. F.; Kessel, C. R.; Brace, H. N. *J. Am. Chem. Soc.* **1979**, *101*, 1874.

[21] Nelsen, S. F.; Kessel, C. R.; Brien, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 702.

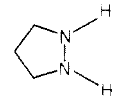
geometry) is not obtainable from such a PE spectrum. Although for some molecules the first rise observed in the PE spectrum is at least close to IP_{ad}, this is certainly not true for hydrazines. Observed PE bandwidths for R_4N_2 are not very sensitive to θ,[18] but $IP_v - IP_{ad}$ must be quite sensitive, because the equilibrium $R_4N_2^{+\cdot}$ geometry has parallel p orbitals ($\theta = 0/180°$) if possible, and changing θ in $R_4N_2^{+\cdot}$ is rather costly in energy, as is discussed below.

The energy difference between the first and second PE bands of R_4N_2 ($IP_2 - IP_1$) is a measure of $|n_+ - n_-|$ and is found to vary between 2.1–2.3 eV for $\theta = 0$ and 180° hydrazines, which are nearly tetrahedral in geometry,[22] and a minimum value of 0.54 ± 0.03 eV for a host of acyclic and *N*,*N*-cycloalkylhydrazines.[18c] Although Figure 2 and INDO/MINDO level calculations on hydrazines predict a crossing of the n_+ and n_- energy levels near 90° (83° for an INDO calculation on idealized tetrahedral tetramethylhydrazine[18c]), this calculated crossing cannot be occurring. The calculations indicate a maximum sensitivity of $IP_2 - IP_1$, near the crossover θ, about 0.18 eV for a 5° change in θ. It is unreasonable to maintain that primary, secondary, and tertiary alkyl R_4N_2 examples would all have the same θ value to within a couple of degrees. The potential curve should have a rather shallow minimum, and steric differences will surely lead to slightly different equilibrium θ values. Instead, there must be an avoided crossing of n_+ and n_-, so that $IP_2 - IP_1$ is actually rather insensitive to θ near the calculated crossover point. This behavior is not really surprising, since the "lone-pair" MOs are not really localized on the nitrogen lone-pair AOs, and electron correlation is ignored in INDO/MINDO level calculations. When θ is not near 90°, $IP_2 - IP_1$ does follow an approximate cos θ relationship,[17,18] although considerable caution must be used in applying a simple equation to give θ from PE data because of rehybridization effects (see below).

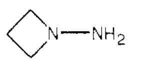
A valuable feature of R_4N_2 PE spectra is that one sees the superposition of spectra for all occupied conformations because the PE timescale is so short. Although this is expected to cause blurring of the observed spectra because the potential well is broad, it leads to a real advantage over other methods for hydrazine conformational analysis. When two conformations of very different θ are occupied, bands for both are observed. This occurs for several examples studied, including derivatives of hexahydropyridazine, pyrazolidine,[17,18] and *n*-aminoazetidine.[19] For the latter two cases, conformational interconversion is expected to be so rapid that NMR observes only averaged conformations.



hexahydropyridazine



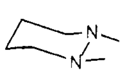
pyrazolidine



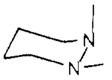
N-aminoazetidine

IP_1 values for R_4N_2 are available from PE work on many examples; for selected cases, see Table I. IP_1 proves to be quite sensitive to alkyl group size. The change in IP_1 as longer *n*-alkyl groups are attached correlates excellently with data for other lone-pair ionizations as alkyl groups are changed.[19a,c] Although $IP_2 - IP_1$ shows the predicted sensitivity to θ when θ is far from 90°, there is conflicting evidence for the predicted destabilization of the HOMO when $IP_2 - IP_1$ is large. Some cases with large $IP_2 - IP_1$ clearly exhibit a low IP_1, such as the $\theta = 0°$ tricyclic compound **17**, which has the lowest R_4N_2 IP_1 yet observed. Some other bicyclic fused compounds which have rather large lone-pair/lone-pair interactions such as **10** and **11** also have low IP_1 values considering the number of attached carbons.

Nevertheless, the qualitative prediction from Figure 2 of a lower IP_1 for large $IP_2 - IP_1$ compounds has major exceptions. Because of the large dependence of IP on alkyl group size, the best example to consider is 1,2-dimethylhexahydropyridazine (**7**), which exists in two conformations with very different θ values, **7ee** ($\theta \sim 180°$) and **7ae** ($\theta \sim 60°$). Their $IP_2 - IP_1$ differences are experimentally 2.26 and 1.04 eV, respectively,[23] the $\theta = 180°$ conformation having a much larger difference, as expected from Figure 2. However, Figure 2 also leads one to expect that **7ee** would have a lower IP_1 than **7ae** by about (2.26–1.04)/2 = 0.61 eV (14 kcal/mol), but their IP_1 values are experimentally the same. The two nitrogen AOs overlap to form two MOs, n_+ and n_-. On the basis of the approximation that destabilization and stabilization of these MOs are equal (as is usual in analyses of this sort[24]), the equality of IP_1 for **7ee** and **7ae** requires that the nitrogen lone-pair AOs of **7ee** lie about 14 kcal/mol lower in energy that those of **7ae**, which is certainly not implied by Figure 2, or indeed by energy-minimized MINDO/3 level calculations on hydrazine itself.[25]

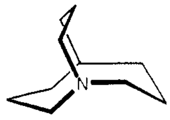


7ee



7ae

This discrepancy bothered us for several years, but recent X-ray crystallographic work has convinced us that the answer lies in a change in nitrogen hybridization as θ is changed in a hydrazine. The $\theta = 180°$ conformation is electronically destabilized, and a hydrazine forced by its alkyl substituents to assume a $\theta = 180°$ conformation should alter its geometry about nitrogen to minimize lone-pair/lone-pair overlap, until a balance is reached between the electronic destabilization and the energy cost of distorting to minimize it. Lengthening the NN bond and bending slightly more at nitrogen tend to do this. Increased bending at nitrogen rehybridizes the lone-pair AOs, and lone-pair hybridization has an important effect on AO energy. MINDO/3 calculations on amines give the result that IP_1 correlates linearly with fractional p character (f_p) in the lone-pair MO, and PE data on triethylamine ($f_p \sim 0.75$) and 1-azamanxane ($f_p \sim 1.0$) suggest an effect of 0.8 eV for going from sp^3 to pure p lone-pair hy-



1-azamanxane

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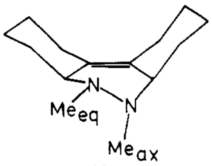
[22] A significantly larger $IP_2 - IP_1$ of 2.53 eV is observed for the θ = 180° conformation of bis(aziridine).[17a]

(23) Schweig, A.; Thon, N.; Nelsen, S. F.; Grezzo, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 7438.

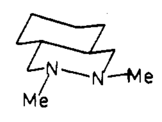
(24) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

(25) W. C. Hollinsed, unpublished results.

bridization in a trialkylamine.[21] The gauche lone-pair hydrazine **18** ($\theta \sim 70°$) has its nitrogens significantly flatter than a simple amine; f_p is 0.79 and 0.82 at the axial and equatorial methyl nitrogens, respectively.[26] In contrast, the two $\theta = 180°$ hydrazines which have had X-ray structural determinations performed (**19** and **12**) have significantly more bent nitrogens, f_p being 0.69–0.70[26] and 0.72,[27] respectively. We argue that similar charges in f_p for the nitrogens of **7** occur, and lead to the 0.61-eV greater stability for the nitrogen AOs of the **7ee** conformation than for the **7ae** conformation required by the experimental PE spectrum of **7**. Sterically imposed flattening at nitrogen will also cause higher f_p values, and consequently low IP_1, as seen for **17** and **11**.[28]



18



19

Despite the complexity of predicting IP_1 for hydrazines (and we will not even go into the evidence for alkyl conformation having a rather minor but easily measurable effect[19c]), the IP_1 value is easily measured by PE spectroscopy. We now turn to consideration of electron removal in the solution phase.

Solution-Phase Electron Removal: $E°'(R_4N_2,R_4N_2^{+}\cdot)$. The thermodynamic ease of electron removal in solution has been measured by CV[29] for many examples of R_4N_2. It is most useful for this discussion to refer all measurements to tetramethylhydrazine; the $\Delta(\Delta G°)$ entries of Table I are values of $\Delta G°(R_4N_2,R_4N_2^{+}\cdot) - \Delta G°(Me_4N_2,Me_4N_2^{+}\cdot)$ in kcal/mol, numerically 23.06 times $\Delta(E°')$. A glance at Table I or Figure 1 shows that $\Delta(\Delta G°)$ has relatively little to do with IP_1, despite the fact that both numbers refer to what is qualitatively the same process, removal of a single electron. The principal reason for this lack of correlation is the time scale of the two experiments. The vapor-phase measurement (IP_1) is very rapid and gives the vertical energy gap, i.e., the energy difference between R_4N_2 and $R_4N_2^{+}\cdot$ in the same geometry as the neutral compound. The solution-phase measurement ($E°'$) involves equilibration of R_4N_2 and $R_4N_2^{+}\cdot$ at the electrode, a far slower process (cation radical lifetimes of tens of milliseconds are required to measure $E°'$), and it corresponds to the adiabatic energy gap, i.e., between R_4N_2 and $R_4N_2^{+}\cdot$ in its equilibrium geometry. The adiabatic and vertical energy gaps are essentially the same for aromatic hydrocarbons, which show PE spectra with vibrational fine structure typically having the 0,0 band the most intense. Under these circumstances, one expects and sees a linear IP_1 vs. $E°'$ plot.

We argue, then, that the poor correlation for hydrazines is a result of a large energy difference between the vertical and adiabatic $R_4N_2^{+}\cdot$ structures. This is shown diagramatically in Figure 3, where ΔG(rel) corresponds to the free energy of relaxation from the vertical to the adiabatic cation radical structure. If we were able to plot $E°'$ vs. IP_{ad} for R_4N_2, we would expect a linear correlation, but when the neutral and radical cation structures differ greatly, as they do for hydrazines, there is virtually no overlap between their wave functions, and no known experiment directly measures IP_{ad}.

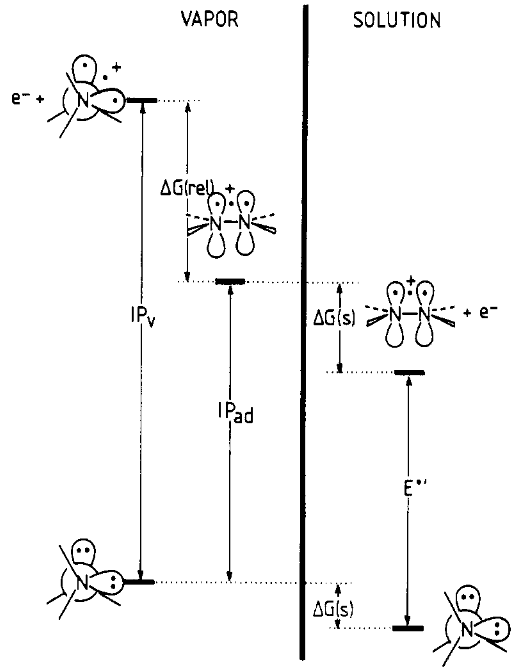


Figure 3. Diagramatic comparison of the relationship of vapor phase ionization potential and solution phase oxidation potential for tetraalkylhydrazines.

The large and variable size of ΔG(rel), which is implied by the scatter of R_4N_2 points in Figure 1, suggests a large geometry change upon electron removal. Much is known about the geometry of neutral hydrazines.[30] They electronically prefer nearly tetrahedral nitrogens, with $\theta \sim 90°$. Obviously, the alkyl groups attached can force the nitrogens out of their preferred geometry, at a cost in energy, and hydrazines are known covering the entire range from $\theta = 0°$ (such as **9** and **17**[18e]) to 180° (such as **7ee**, **8**, and **19**). The nitrogens can be substantially more bent than tetrahedral (as in **13** and **14**), or substantially flattened (as in **11**[28]).

Experiments of several types have shown that the preferred geometry for hydrazine radical cations is olefin-like, i.e., having the nitrogens and the four attached carbons coplanar, and hence two parallel p orbitals interacting to form an olefin-like two-atom π system which contains two bonding and one antibonding electrons. ESR studies have indicated that unconstrained examples of $R_4N_2^{+}\cdot$ have a planar equilibrium geometry[31–34] for which the nitrogen splitting a(N) has the smallest value. Bending at nitrogen introduces s

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[26] Nelsen, S. F.; Hollinsed, W. C.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 4461.

[27] Nelsen, S. F.; Hollinsed, W. C.; Kessel, C. R.; Calabrese, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 7876.

[28] Nelsen, S. F.; Hollinsed, W. C.; Grezzo, L. A.; Parmelee, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 7347.

[29] For introductory discussions of cyclic voltammetry, see: (a) Cauquis, G.; Parker, V. D. "Organic Electrochemistry"; Baizer, M. M., Ed.; Marcel Dekker: New York, 1973; p 115. (b) Fry, A. J. "Synthetic Organic Electrochemistry"; Harper and Row: New York, 1973; p 79.

[30] For a review on hydrazine conformations, see: Shvo, Y. "Chemistry of Hydrazo, Azo, and Azoxy Groups"; Patai, S., Ed.; Wiley: New York, 1975; Part 2, pp 1017–1095.

[31] (a) Marquardt, C. L. *J. Chem. Phys.* **1970**, *53*, 3248. (b) Reilly, M. H.; Marquardt, C. L. *Ibid.* **1970**, *53*, 3257.

[32] Atkinson, T. V.; Bard, A. J. *J. Phys. Chem.* **1971**, *75*, 2043.

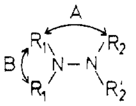
[33] Smith, P.; Stevens, R. D.; Kaba, R. A. *J. Phys. Chem.* **1971**, *75*, 2048.

[34] (a) Nelsen, S. F.; Weisman, G. R.; Hintz, P. J.; Olp, D.; Fahey, M. R. *J. Am. Chem. Soc.* **1974**, *96*, 2916. (b) Nelsen, S. F.; Echegoyen, L. *Ibid.* **1975**, *97*, 3530.

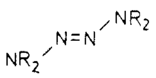
character into the odd-electron MO, and because s orbitals have a non-zero density near the nucleus and a(N) is proportional to spin density near the nucleus, bending at nitrogen increases a(N). Thus $14^{+}\cdot$, which cannot flatten very much because of its caged structure, has an a(N) value about twice as large as unconstrained examples of $R_4N^{+}\cdot$ such as $1^{+}\cdot$.[20]

Because bending at nitrogen is quite easy, however, the observed a(N) is a time average over occupied vibrational levels.[35] When the alkyl groups attached impose a greater stability for forms bent at nitrogen, the equilibrium geometry is bent, as shown by variable temperature ESR studies.[34] Even for $9^{+}\cdot$, a relatively high a(N) example, however, flattening at nitrogen is far easier in the radical cation than in the neutral form; the double nitrogen inversion barrier for $9^{+}\cdot$[34] is only about one-quarter as large as that for neutral 9.[36] A large geometry charge for electron removal has been documented by obtaining X-ray crystallographic structures for 12 and $12^{+}\cdot PF_6^{-}$.[27] Although neutral 12 is forced into the electronically destabilized $\theta = 180°$ conformation by its bulky alkyl groups, the nitrogens are more bent than tetrahedral geometry, while the nitrogens of $12^{+}\cdot$ are coplanar with the four α carbons and the NN bond length is a surprising 15% shorter.[27]

The structural change upon electron removal results in significantly different steric interactions between the alkyl groups in neutral and radical cationic R_4N_2, which naturally affects $E°'$, which is the free-energy difference between these two species. The steric interactions between syn substituents on adjacent nitrogens (see interaction A in II) is increased, but that between groups on the same nitrogen is decreased (see B in II). These factors are at least largely separated in the structurally related 2-tetrazenes III, where the A interaction is minimized by inclusion of the azo linkage between the trisubstituted nitrogens.[19c] This allows determination of the relative sizes of the effect of alkyl group homologation in the vapor phase and in solution. A plot of $E°'$ vs. IP_1 for n-alkyl III gives a straight line with a slope of 0.22, substantially smaller than the 0.9 slope for aromatic hydrocarbons.



II



III

Changing IP_1 by changing alkyl group size is clearly quite different from changing it by altering the size of the π system, as was done for the aromatic compounds. As Taft and co-workers have pointed out,[37] the principal factor making larger alkyl groups lower IP_1 is alkyl group polarizability, a factor which essentially disappears in solution where solvent is available to be polarized. We cannot quantitatively separate alkyl group size effects from solvation change effects, but the sum of the two for tetra-n-alkylhydrazines leads to an $E°'$ vs. IP_1 slope of 0.15, with a slight tailing up of the line for long alkyl groups (i.e., at the low IP_1 end; note the same $E°'$ for 2 and 3 despite a 6.4 kcal/mol lower IP_1 for 3).

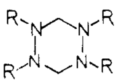
The small dependence of $E°'$ on IP_1 as alkyl group size is changed makes changes in steric interactions dominate the $E°'$ values observed, and the principal structural effects on $E°'$ are clear even when the small IP_1 effect is ignored and can be seen just by examining the $\Delta(\Delta G°)$ column of Table I. The di-*tert*-butyl compound 4 is 5.5 kcal/mol harder to oxidize than 1 because A destabilization dominates B stabilization (see II). The positive increments in $\Delta(\Delta G°)$ for R_4N_2 containing six-membered rings and negative ones for five-membered rings are a result of torsional strain changes, as has been developed fully elsewhere.[19c,d]

The most important conclusion from $E°'$ studies involves the size of destabilizations which occur when the alkyl groups force $R_4N_2^{+}\cdot$ out of their preferred, olefin-like geometry. Large destabilization results when the NN bond is forced to be twisted, as in $15^{+}\cdot$ and $16^{+}\cdot$. 16 has $\Delta(\Delta G°) > 12.9$ kcal/mol, corresponding to an $R_4N_2^{+}\cdot$ destabilization of >15 kcal/mol when HOMO energy is taken into account.[20] The $E°'$ results are, however, completely consistent with the ESR-derived result that a modest amount of bending at nitrogen cost little energy. Thus high a(N) $R_4N_2^{+}\cdot$ examples like $9^{+}\cdot$ and $17^{+}\cdot$ are thermodynamically rather easy to form. On the other hand, caged hydrazine 14, which can relax very little upon electron removal, is quite difficult to form, $\Delta(\Delta G°)$ being +11.1 kcal/mol (HOMO-adjusted destabilization of 13.8 kcal/mol[20]), so forcing enough bend in $R_4N_2^{+}\cdot$ does become quite costly in energy. The result of easy bend at nitrogen, but difficult twist about the NN bond, is, we argue in the last section, important for understanding the rates of electron transfer from hydrazines.

Kinetics of the R_4N_2–$R_4N_2^{+}\bullet$ Electron Transfer

Electron Exchange Rates in Solution. Since electron exchange rates depend on reaction exothermicity, it is common to study radical ion–neutral exchange between identical partners, so $\Delta G°$ is zero, using ESR line broadening to detect exchange.[4] Much work has been done on intramolecular exchange within monoanions having two identical aromatic systems linked by an aliphatic chain.[38] Electron exchange is found to be fast on the ESR time scale when a single methylene group links the substituents and free ions or loose ion pairs are involved, but tight ion pairing can slow electron–cation exchange markedly.

In contrast, the monocations of bishydrazine 20 (R = Me, Et) show no evidence for ESR line broadening in butyronitrile at room temperature,[39] and the spectrum observed is clearly that with the odd electron localized in one hydrazine unit. Although the ESR spectra of $R_4N_2^{+}\cdot$ are very complex because of second-order splitting[34b] and not very favorable for detecting broadening, this result requires the exchange rate to be much less than 4×10^7 s^{-1}.



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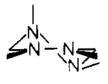

$21^{+}\cdot$

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(35) (a) Lisle, J. B.; Williams, L. F.; Wood, D. E. *J. Am. Chem. Soc.* **1976**, *98*, 227. (b) Krusic, P. J.; Mealen, P. *Ibid.* **1976**, *98*, 226. (c) Krusic, P. J.; Bingham, R. C. *Ibid.* **1976**, *98*, 230.

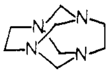
(36) Kintzinger, J. P.; Lehn, J. M.; Wagner, J. *J. Chem. Soc., Chem. Commun.* **1967**, 206.

(37) Taft, R. W.; Taagepera, M.; Abboud, J. L. M.; Wol, J. E.; DeFreez, D. J.; Hehre, W. J.; Bartmess, J. E.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 7765.

(38) Reference 1, p 71 ff.

(39) Nelsen, S. F.; Hintz, P. J.; Buschek, J. M.; Weisman, G. R. *J. Am. Chem. Soc.* **1975**, *97*, 4933.

We suggested that the electron transfer rate is so low for these species because the structure resembles **21**$^{+\cdot}$, with one pair of nitrogens flattened into the olefin-like geometry of $R_4N_2^{+\cdot}$, but the other pair of nitrogens retaining the near-tetrahedral geometry of R_4N_2. Electron transfer should require flattening at both nitrogens of the neutral hydrazine, which is quite costly in energy. Flattening at one nitrogen of a hydrazine requires about 13 to 7 kcal/mol in energy at room temperature, depending on the degree of lone-pair/lone-pair interaction in the flattened form,[40] and substantial flattening at both nitrogens would clearly make electron transfer slow on the ESR time scale. The slow electron transfer in **21**$^{+\cdot}$ makes a great contrast with that in **22**$^{+\cdot}$, which is rapid on the ESR time scale even at −100 °C in butyronitrile,[41] although **22**$^{+\cdot}$ has two sets of two nitrogens linked by methylene groups, as does **20**$^{+\cdot}$. The proton splittings of **22**$^{+\cdot}$ are inconsistent with a delocalized species having all four nitrogens equivalent,[41] as is its electronic absorption spectrum.[42] This species is best described as **23**$^{+\cdot}$, with rapid electron transfer between the two sets of nitrogens.[12c] The caged structure of **23**$^{+\cdot}$ forces a low activation energy for intramolecular electron transfer, in contrast to bishydrazine **21**$^{+\cdot}$.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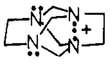
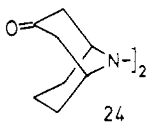

23$^{+\cdot}$

Intermolecular electron-transfer self-exchange has $k_2 > 7 \times 10^8\ M^{-1}\ s^{-1}$ at room temperature for the relatively few radical cation cases reported.[43] Once again, R_4N_2,$R_4N_2^{+\cdot}$ exchange is anomalously slow. We failed to detect ESR line broadening for **9**/**9**$^{+\cdot}$ mixtures,[39] where $k_2 < 10^7\ M^{-1}\ s^{-1}$. The Bredt's rule protected bis(bicyclic) hydrazine **24** failed to show NMR line broadening at 0.1 M in the presence of 4.8×10^{-3} M **24**$^{+\cdot}$ in 1:2 $CD_3CN/CDCl_3$,[44] requiring that $k_2 < 6 \times 10^2\ M^{-1}\ s^{-1}$. In contrast, ESR line broadening is easily detectable for mixtures of **25**· and **25**$^{+}$,[45] so k_2 must be several orders of magnitude larger. We argue that the key difference between R_4N_2–$R_4N_2^{+\cdot}$ self-transfer, which is very slow, and **25**·–**25**$^{+}$ self-transfer, which is quite fast, is that little geometry changes takes place in the latter case, for the odd electron is in a nearly pure p orbital at the nitrogens in **25**· by ESR studies.[46] Interestingly, Michejda and co-workers reported very rapid exchange between $1^{+\cdot}I_3^-$ and 1, $k_2 = 9 \times 10^9\ M^{-1}\ s^{-1}$ [47] in solvents of intermediate polarity. This is certainly very different than results with ClO_4^-, $SbCl_6^-$, and BF_4^- counterions reported above, although what is involved is unclear.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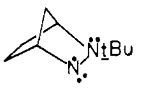
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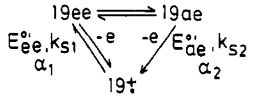
Heterogeneous Electron Transfer. Electrochemical reversibility requires not only long lifetimes for both forms of a redox couple but also heterogeneous electron-transfer rates which are fast compared to the time scale of the experiment, CV in this work. If the heterogeneous electron-transfer rate constants, k_s, are too small, the peak potential difference ($E_p^{ox} - E_p^{red}$) in a CV experiment increases from the reversible value of 57 mV at room temperature, and $E°'$ is no longer exactly $(E_p^{ox} - E_p^{red})/2$.[29] Hydrazine electron-transfer rates are almost slow enough to make determination of $E°'$ by CV difficult. Their CVs are clearly quasi-reversible (heterogeneous rate constants noticeably slow on the CV time scale) at glassy carbon electrodes, somewhat faster at platinum, and (luckily) nearly reversible at gold,[48] where values of $E_p^{ox} - E_p^{red}$ in the 50–200 mV/s scan range we usually use are typically 60–85 mV. Inasmuch as $E°' \simeq (E_p^{ox} - E_p^{red})/2$ is accurate to the 10-mV reproducibility of our data, such $E°'$ values were reported in the work discussed above.

Scheme I



A particular significant aspect of the CV study of hydrazines has been the demonstration that k_s is sensitive to dihedral angle θ. Six-ring hydrazines which have both **ae** and **ee** forms such as **7** and **19** show reversible room temperature CV curves, which look like other cases, but at low temperature and/or fast scan rates, a second, irreversible wave appears at more positive potential than the nearly reversible wave. It was demonstrated empirically that the second, irreversible wave is caused by the **ae** form and that the electrode is merely sampling the equilibrium ratio of **ee** and **ae** hydrazines present in the bulk solution.[49] Although the position of the irreversible wave is very surface dependent, quantitative fit to reaction Scheme I is observed. This allows conformational analysis of six-ring hydrazines by low-temperature CV, a method complementary to ^{13}C NMR, which in many cases gives additional information when these two are used together.[40,49] The resolution of the CV curve into separate peaks for **ee** and **ae** conformations must be based on a much slower k_{s2} than k_{s1} because the $E°'$ values for **ee** and **ae** are nearly identical on a volt scale, and the **ae** peak lies positive of the **ee** peak even in cases where $E°'_{ae}$ is negative of $E°'_{ee}$ (i.e., when K_e = [**ae**]/[**ee**] is less than 1). The reduction is completely kinetically controlled, the radical being reduced only to the **ee** conformation, even when the **ae** conformation is thermodynamically stabler.

We argue that the far easier bend than twist of $R_4N_2^{+\cdot}$ provides the qualitative explanation for this result. The transition state for k_{s2} should be twisted about the NN bond as well as bent at N, while that for k_{s1} should be untwisted because the lone pairs are coplanar in **ee**. Similarly, addition of an electron generates only the coplanar lone-pair **ee** conformation from the radical cation.[50]

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(40) Nelsen, S. F. *Acc. Chem. Res.* **1978**, *11*, 14.

(41) Nelsen, S. F.; Buschek, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 6424.

(42) Private communication from E. Haselbach, R. Gschwind, and U. Klemm.

(43) Reference 1, pp 85–86.

(44) Unpublished work of C. R. Kessel.

(45) Unpublished work of W. P. Parmelee.

(46) Nelsen, S. F.; Landis, R. T., II. *J. Am. Chem. Soc.* **1974**, *96*, 1788.

(47) Romans, D.; Bruning, W. H.; Michejda, C. J. *J. Am. Chem. Soc.* **1969**, *91*, 3859.

(48) Kinlen, P. J.; Evans, D. H.; Nelsen, S. F. *J. Electroanal. Chem.* **1979**, *97*, 265.

(49) (a) Nelsen, S. F.; Echegoyen, L.; Evans, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 3530. (b) Nelsen, S. F.; Echegoyen, L.; Clennan, E. L.; Evans, D. H.; Corrigan, D. A. *Ibid.* **1977**, *99*, 1130. (c) Nelsen, S. F.; Clennan, E. L.; Evans, D. H. *Ibid.* **1978**, *100*, 4012. (d) Evans, D. H.; Nelsen, S. F. "Characterization of Solutes in Nonaqueous Solvents"; Mamantov, G., Ed.; Plenum Press: New York, 1978, 131.

Concluding Remarks

The properties of the R_4N_2–$R_4N_2^{+\cdot}$ electron transfer include thermodynamics which are not dominated by HOMO energy level, exceedingly slow homogeneous electron transfer rate, and conformation-dependent heterogeneous electron-transfer rate. All of these properties have been argued to be a result of the large geometry change which occurs upon electron removal, a feature which is of course shared by many other types of compounds. The advantage of R_4N_2 for study of these phenomena, which in certain aspects resemble "inner sphere" electron transfers in transition-metal systems, is the great degree of control over both the HOMO energy level and the degree of geometry change exerted by altering the geometry of the four alkyl substituents, which only interact weakly with the two nitrogen lone pair system.

It is a pleasure to thank the many students who carried out the work discussed here: P. J. Hintz, R. T. Landis, II, J. M. Buschek, G. R. Weisman, Dr. L. Echegoyen, E. L. Clennan, V. E. Peacock, W. C. Hollinsed, C. R. Kessel, and W. P. Parmelee, as well as Dr. J. C. Calabrese, without whom the X-ray work could not have been done, and Professor D. H. Evans, whose efforts have allowed us to use electrochemical techniques profitably, and his students, D. A. Corrigan and P. J. Kinlen. The work reported has been supported by the National Science Foundation, the Petroleum Research Fund, administered by the American Chemical Society, and the Wisconsin Alumni Research Foundation.

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(50) A kinetic equivalent of Scheme I would place a twisted radical cation, (**19ae**)$^{+\cdot}$, between **19ae** and **19**$^{+\cdot}$. If this intermediate only relaxed to **19**$^{+\cdot}$ and never could be reduced to **19**, the CV curves would look the same. Our principal reason for preferring Scheme I is not only its greater simplicity but also the fact that when we make a twisted intermediate (**16**$^{+\cdot}$), very rapid deprotonation occurs because of the high energy of the twisted radical cation. Our results require that if (**19ae**)$^{+\cdot}$ is formed, it gets to (**19**)$^{+\cdot}$ in high yield. This is not inconceivable, but at present we feel there is insufficient evidence for a twisted radical cation to justify postulating one.

Solvated Electron Structure in Glassy Matrices

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Solvated electrons were probably first produced by chemists when Weyl in 1864 dissolved sodium in liquid ammonia to generate a beautiful blue color.[1] However, this color and its spectrum were not assigned to solvated electrons as such until 1908.[2] Since that time extensive studies of these stable solvated electrons in liquid ammonia by optical and electron magnetic resonance spectroscopy, by a variety of other physical measurements, and by extensive theoretical calculations have revealed many facets of their physical characterization and reactivity.[3] However, the detailed *geometrical* structure of these solvated electrons has not yet been deduced.

In 1962 a solvated electron in water was discovered as a transient optical spectrum in the visible produced by pulse radiolysis.[4] In the same year a very similar, stable spectrum was found by radiolysis of an alkaline aqueous glass at 77 K and was assigned to a trapped electron.[5] Subsequent work has shown that transient solvated electrons may be produced in various liquids, including alcohols, ethers, amines and alkanes, and that trapped, solvated electrons are also formed by inducing molecular reorientation in *glassy* matrices of these liquids at 77 K.[6]

Many aspects of solvated electrons have received[7] and continue to receive[8] much study. Their reactivity was first extensively investigated mainly in aqueous systems.[9] We early pointed out that entropic effects seem to control solvated electron reactivity in both liquid and glass media, implying the importance of an electron-tunneling mechanism.[10] Recent comprehensive kinetic studies in glassy matrices appear to firmly establish the importance of electron tunneling for solvated electrons.[11] Investigations of optical absorption and photoconductivity spectra in glassy matrices in our laboratory have established the broad outlines of the electronic energy level structures of solvated electrons in both aqueous and organic systems.[6] Concurrent development of theoretical models of solvated electrons have led to a semicontinuum potential model which has proven modestly successful in explaining the electronic energy level structure.[12] This theoretical model has also made certain limited predictions regarding geometrical structure. However, detailed experimental data on the *geometrical* structure of solvated electrons have been lacking until very recently. In this Account

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