For 2N, k_z = 0: 12 (1), 4 (1), 0 (1). k_z = 1: 19 (1), 1 (1). k_z = 2: 4 (1). We note that the number of components and shifts are the same for 2N as for 4H, but that the intensities are different.

(5) For a review, see P. D. Sullivan and J. R. Bolton, *Advan. Magn. Reson.*, **4**, 39 (1970).

(6) For a good discussion of the temperature variation of β splittings as an indication of conformation, see P. J. Krusic, P. Meakin, and J. P. Jesson, *J. Phys. Chem.*, **75**, 3438 (1971).

(7) M. Sevilla and G. Vincow, *J. Phys. Chem.* **72**, 3647 (1968).

(8) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(9) D. E. Wood, L. F. Williams, R. F. Sprecher, and W. A. Lathan, *J. Am. Chem. Soc.*, **94**, 6241 (1972).

(10) (a) M. C. R. Symons, *Mol. Phys.*, **24**, 461 (1972); (b) *Tetrahedron Lett.*, 207 (1973); (c) D. Griller and K. U. Ingold, *J. Am. Chem. Soc.*, **95**, 6459 (1973).

(11) For a discussion of application of the $a(H_A)/a(H_B)$ ratio to conformational analysis, see S. F. Nelsen and J. P. Gillespie, *J. Am. Chem. Soc.*, **95**, 2940 (1973), and references therein.

(12) G. A. Russell, G. R. Underwood, and D. C. Lini, *J. Am. Chem. Soc.*, **89**, 6636 (1967).

(13) M. J. S. Dewar and W. B. Jennings, *J. Am. Chem. Soc.*, **95**, 1562 (1973).

(14) V. Malatesta and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 3949 (1974).

(15) T. V. Atkinson and A. J. Bard, *J. Phys. Chem.*, **75**, 2048 (1971).

(16) P. Smith, R. D. Stevens, and R. A. Kaba, *J. Phys. Chem.*, **75**, 2048 (1971).

(17) The fact that a(N) average increases[15] in going from hydrazine (11.5) to methylhydrazine (12.25) to dimethylhydrazine (12.87), in spite of increased hyperconjugation, suggests that the geometry is indeed changing. Changes in amount of hyperconjugation would be expected to make a(N) decrease in this series. Both effects should be minimized for tetralkylhydrazines, and we have ignored them.

(18) The difference between $(1 - X_{Me-H})^2$ and $(1 - 2X_{Me-H})$ is too small to be significant here but, when more accurate data are in hand, the expressions of the former form work better. See R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963); and S. F. Nelsen and J. M. Buschek, *J. Am. Chem. Soc.*, **96**, 2392 (1974).

(19) R. W. Taft in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1956, p 619.

(20) S. F. Nelsen and G. R. Weisman, *Tetrahedron Lett.*, 2321 (1973).

Electron Transfer between Tetraalkylhydrazine Radical Cations and Tetraalkylhydrazines

S. F. Nelsen,* P. J. Hintz, J. M. Buschek, and G. R. Weisman

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706.

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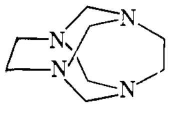
Abstract: The radical cations of both tetramethyl and tetraethyl *sym*-hexahydrotetrazine have the odd electron localized in one hydrazine unit, and intramolecular electron transfer between the methylene bridged hydrazine units is slow on the ESR time scale. The intermolecular electron transfer rate is also unusually slow between 3,3,7,7-tetramethyl-1,4-diazabicyclo-[3.3.0]octane and its radical cation, because less than 0.7 g of line broadening is observed when the ESR spectrum of the radical cation is recorded in a solution over 0.8 *M* in the neutral hydrazine.

We recently reported[1] that the radical cation of tetraazatricyclododecane (**1**) gives an ESR spectrum showing splittings for four equivalent nitrogens and two sets of eight equivalent hydrogens at −100°. Although all that is required by this ESR result is a low activation energy for electron transfer among the nitrogens, we argued from the low $E_{1/2}$ for electrolytic oxidation that the charge was actually delocalized over all four nitrogens in **1**$\cdot^+$. The structure of **1** shares with that of Dabco (**2**) the feature of having ethylenediamine units held with their lone pair (C–C) lone pair units approximately colinear. Substantial changes from this geometry make large changes in the amount of lone pair–lone pair interaction as measured by photoelectron spectroscopy[2] and cause the radical cations to have such short lifetimes that their re-reduction is not detectable in a cyclic voltammetry experiment.[3] Because of the unusual effect of methylene bridging to enable 1,3 interactions between two units to occur in **1**, we thought it would be of interest to examine the monocations of *sym*-hexahydrotetrazines **3**, which incorporate two methylene-bridged tetraalkylhydrazines.



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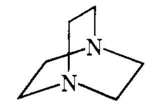

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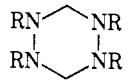

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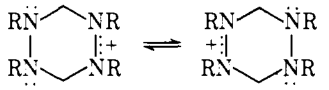
Results

Hexahydrotetrazine ESR Spectra. From the known ESR spectra of six ring hydrazines,[4] it is easy to distinguish whether the odd electron is localized in one hydrazine unit, which will give a spectrum with two equivalent nitrogen splittings and a(N) near 13 G, from that of a four nitrogen delocalized or rapidly equilibrating **3**$\cdot^+$ ⇄ **3′**$\cdot^+$ system, which would have four equivalent nitrogens with a splitting about half as large. Both **3**$\cdot^+$ (R = CH_3) and **3**$\cdot^+$ (R = CH_2CH_3) give ESR spectra of the former type at room temperature, clearly demonstrating that intramolecular electron transfer is slow. Similar spectra were observed both by electrolytic oxidation in acetonitrile, and chemical oxidation in butyronitrile. The splittings observed appear in Table I. The ESR spectrum of **3**$\cdot^+$ (R = CH_2CH_3) showed only rather broad lines, and we were unable to resolve the difference between a(N) and a(CH_2). The observation of a four hydrogen quintet with the splitting expected for a 1,2-diethylhydrazine[4] and of such a large nitrogen splitting clearly requires localization of the odd electron in only one hydrazine unit, however. For **3**$\cdot^+$ (R = CH_3), we could resolve the difference between a(CH_3) and a(N). Because of the accidental equality of a(CH_2)–a(N) and a(N)–a(CH_3), however, most of the lines observed consist of overlapping components having different magnetic quantum numbers. Although the relative intensities of the observed lines at room temperature were fairly close to those expected on the basis of the degeneracies of the lines, large deviations appeared at low temperatures. As expected from the low temperature ESR spectra of other tetraalkylhydrazine radical cations,[4] anisotropic line broadening seriously



3$\cdot^+$ 3′$\cdot^+$

Table I. Hyperfine Splittings for *sym*-Hexahydrotetrazine Radical Cation ESR Spectra[a]

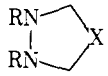
Compd	a(N)	a(CH$_2$)	a(alkyl)
$3\cdot^+$ (R = CH$_3$)	14.56 (2)	15.67 (4)	13.43 (6)
$3\cdot^+$ (R = CH$_2$CH$_3$)	ca. 12.9 (2)	ca. 12.9 (4)	8.6 (4)

[a] At room temperature in butyronitrile, tris(*p*-bromophenyl)aminium hexachloroantimonate as oxidant.

broadens the $M_N \neq 0$ components, and there is also an alternating line width effect broadening the M_{CH_2} = odd lines. Because of the great amount of overlap and complexity of the spectra, we were unable to analyze these effects quantitatively and were unable to reach the low temperature limit for the methylene splittings. The alternating line width effect is expected for the localized cation **3**$\cdot^+$ because of the presence of the second, unoxidized hydrazine group in the ring. Even though rapid double nitrogen inversion occurs at the oxidized hydrazine, inversions should be much slower in the unoxidized hydrazine portion of the molecule,[5] leading to inequality of the methylene hydrogen splittings at low temperature. We were unfortunately not able to investigate **3**$\cdot^+$ at high temperatures because both examples were too unstable.

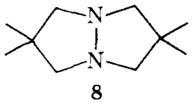
The lack of rapid electron transfer between the two hydrazine units of **3**$\cdot^+$ is a rather surprising result (see Discussion) so we attempted some experiments to determine whether the hydrazine–hydrazine radical cation system is unusually slow in intermolecular electron transfers, as well as intramolecular ones.

Cyclic Voltammetry. A slow enough electron transfer from a hydrazine to an anode would result in quasi-reversibility[6] and consequent broadening of the cyclic voltammetry (CV) waves. In our earlier CV study of tetraalkylhydrazine oxidation,[7] we noted that diisopropyl five ring hydrazines **4** and **5** gave somewhat larger peak-to-peak wave separations (ΔE_p values of 120 and 130 mV, respectively) than their ethyl analogs **6** and **7** (85 to 70 mV, respectively). This suggested that electron transfer might be slower for **4** and **5** than for **6** and **7**, and that quasi-reversibility might have been detected for the isopropyl compounds. Closer examination showed, however, that at least part of the extra broadening previously observed was caused by surface effects since frequent cleaning of the gold electrode enabled us to observe ΔE_p values between 80 and 90 mV, much closer to the 57 mV expected for a completely electrochemically reversible oxidation. We abandoned our attempts to determine heterogeneous transfer rates from the CV wave shape because of these serious surface contamination phenomena.



4, R = *i*-Pr; X = CH$_2$
5, R = *i*-Pr; X = O
6, R = Et; X = CH$_2$
7, R = Et; X = O

Homogeneous Electron Transfer Rates. We next turned our attention to homogeneous electron transfer between neutral hydrazine and hydrazine radical cation. In recent studies by the groups of Bard[8] and Brunning,[9] rate constants were measured for a number of neutral cation pairs by fast exchange limit experiments. We employed **8** in similar studies, because it has (for a tetraalkylhydrazine radical cation) rather few lines in its ESR spectrum. Surprisingly, electrolytic oxidation of a 0.65 *M* solution of **8** did not lead to collapse of the hyperfine structure of **8**$\cdot^+$. Since all of Bard and Bruning's systems were well into the fast exchange limit (collapsed hyperfine) at such high concentration of neutral species, it is clear that the rate constant for homogeneous electron transfer for **8**–**8**$\cdot^+$ is far below the 3×10^8 to 6×10^9 l./mol sec range of their compounds. We were unable, unfortunately, to attain narrow line widths for **8**$\cdot^+$, perhaps because of a combination of unresolved methyl splittings, unresolved second-order splittings in the intense lines, and instrumental broadening at the high modulation amplitudes (0.4 G) necessary for observation of the outer line. Nevertheless, we observed a line width of 0.73 ± 0.02 G for the outer line of **8**$\cdot^+$, generated both by electrolytic oxidation of a 10^{-3} *M* solution of the hydrazine and by oxidation of a 0.83 *M* solution to a similar radical concentration. This requires k for **8**–**8**$\cdot^+$ intermolecular electron exchange to be less than ca. 10^7 l./mol sec since ΔH, the line broadening due to electron exchange, is given by[8]



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$$\Delta H = (1 - \pi)\,(N)k/1.52 \times 10^7$$

where $(1 - \pi)$ is a statistical correction having a value of 1.0 for the outer line used, and N is the concentration of neutral hydrazine.

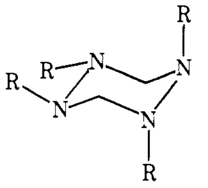
Discussion

The ESR spectra definitely demonstrated that both **3**$\cdot^+$ (R = CH$_3$) and **3**$\cdot^+$ (R = CH$_2$CH$_3$) have the odd electron localized in one hydrazine unit. This result is consistent with the earlier CV study,[7] in which the six ring bishydrazines had higher oxidation potentials than dimethylhexahydropyridazine, as would be expected for the localized cation, since NCH$_2$ substituents on a hydrazine would be electron withdrawing compared with CCH$_2$ substituents.

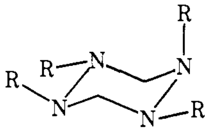
Additionally, the ESR result shows that electron transfer between the hydrazine units is slow on the ESR time scale. The ESR spectrum would be maximally broadened when electron transfer occurs with a rate comparable to Δa Hz [where Δa is the difference in coupling constants for the exchanging splittings, about $2.8 \times 10^6 a$ (gauss) Hz in our case since splittings in the hydrazine unit not bearing the positive charge are too small to observe]. The lack of intensity distortions in the spectrum of **3**$\cdot^+$ indicates that the exchange rate is much less than about 4×10^7 Hz. This result is rather unusual since intramolecular electron transfers between equivalent sites bridged by methylene groups are usually rapid on the ESR time scale. The most studied cases have been those of electron transfer between aromatic rings in radical anions. Transfer is fast in diphenylmethane anion[10] and the 4,4′-dinitro compound[11] and, when the rings are connected by two alkyl chains in the paracyclophanes, electron transfer remains fast with two and three methylene connecting bridges but becomes slow in [4.4]paracyclophane anion.[10] Interesting results on nitro-substituted dibenzobicyclo[2.2.2]octyl and triptycene anions, which are substituted ortho bis-bridged aromatic systems, have been reported by Terabe and Konaka.[12] They found several cases which showed rapid or intermediate electron transfer rates and one in which the electron was apparently localized in one ring on the ESR time scale. The rate of electron transfer is strongly influenced by ion pairing effects, as Gerson and coworkers have found in several cases, including most recently, spirobifluorene radical anion.[13] The high homogeneous electron transfer rates for several radical cation–neutral systems[8,9] suggest that similar intramolecular transfer rates would be observed in radical cationic systems, although such experiments have not been done.

It is, then, unusual that slow electron transfer is observed between the bismethylene bridged hydrazine units of $\mathbf{3}^{\cdot +}$ in polar solvents at room temperature, and we believe that it is a definite indication that some property of the hydrazine–hydrazine radical cation electron transfer must be responsible for this result. That this process is also remarkably slow intermolecularly is indicated by the failure of the $\mathbf{8}$–$\mathbf{8}^{\cdot +}$ system to be in the fast exchange region at over 0.8 *M* concentration of **8**.

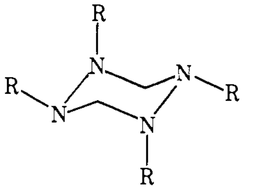
The conformations of **3** (R = CH_3) and **3** (R = CH_2CH_3) have been elucidated by Katritzky and coworkers using dipole moments and NMR,[14] and **3** (R = CH_3) is now known to exist as a rapidly equilibrating mixture of **3A** and **3B**, whereas **3** (R = CH_2CH_3) is a 80:20 mixture of **3C** and **3A**/**3B**. ESR evidence for methyl-substituted hexahydropyridazine radical cations indicated that these species actually exist in boat-like conformations.[15] Large conformational differences clearly must exist between the $\theta \sim 60$ or 180° conformations in neutral **3** molecules, and the $\theta \sim 0°$ conformation of $\mathbf{3}^{\cdot +}$ (θ is the lone pair–lone pair dihedral angle).



3A

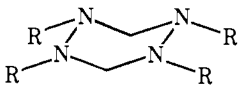


3B



3C

The case of $\mathbf{3}^{\cdot +}$ is in direct contrast to that of $\mathbf{1}^{\cdot +}$, in which the cation actually assumes an intermediate geometry in which all four nitrogens are equivalent. Although this requires a conformational change since $\mathbf{1}^{\cdot +}$ is presumably in the eclipsed D_{2d} conformation and **1** seems certain to be in the expected, torsionally twisted S_4 conformation,[1] this conformational change is not very costly in energy since, even in neutral **1**, interconversion of the two S_4 conformations is rapid on the NMR time scale at −90°, requiring it to have a low activation energy.[16] In contrast, for $\mathbf{3}^{\cdot +}$ to have four equivalent nitrogens, or to have both hydrazine units in $\theta = 0°$ conformations, so that electron transfer would not require an accompanying change in θ, $\mathbf{3}^{\cdot +}$ would need to achieve conformation **9**, which would clearly involve considerable nonbonded interaction strain. Apparently, the energy saving in increased delocalization does not equal the cost in conformational strain, for the positive charge is localized in one hydrazine unit.



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One possible reason for an unusually slow electron transfer rate in hydrazines is the large conformational change involved in going from hydrazine to hydrazine cation radical. Tetraalkylhydrazines are approximately tetrahedral at nitrogen and possess lone pair–lone pair angles (θ) of near 90°,[17] unless cyclic substituents are present which force other rotation angles to be assumed.[18] Tetraalkylhydrazine radical cations possess θ near 0° and are considerably flatter at nitrogen than the neutral compounds, although the degree of bending appears to be quite sensitive to structure.[4] Great geometrical changes must take place during the electron transfer then, and we suggest that the necessity of such geometrical changes occurring could result in substantial lowering of the electron transfer rate compared with most compounds, in which geometrical changes during electron transfer are much less important.

The idea that a large conformational change would result in a slow electron transfer is not a new one and has been previously used to rationalize the slow heterogeneous electron transfer rate for reduction of cyclooctatetraenes.[19-21] Such effects are also apparent in the slow rates for heterogeneous two-electron transfers observed for azacyclooctatetraenes[22] and perhaps for some dimethylamino-substituted butadienes,[23] although the latter case is less certain because observation of the effects on the CV which may be caused by a slow rate is dependent upon the electrode composition. Since the CV waves of tetraalkylhydrazines are reversible (or nearly reversible),[7] the rate slowing is clearly not as pronounced for hydrazine oxidation as it is for cyclooctatetraene reduction.

Another possibility for the apparent slow electron transfer rate of hydrazines is that it is caused simply by the high degree of charge localization in hydrazine radical cations. The positive charge is localized on the two nitrogens, except for hyperconjugation effects. Hale[24] has summarized a simplified theoretical treatment in which the reorganization energy, the work required to take the atoms and molecules in the environment of the reactant from their equilibrium positions to their equilibrium positions in the product, is considered to consist of two terms, "inner" and "outer." The "inner" term refers to bond length and angle changes accompanying electron transfer and would be the one affected by the conformational change arguments discussed above. The "outer" term is caused by electrostatic contributions. According to the theory,[24] the "inner" term is an order of magnitude larger for cyclooctatetraene than it is for planar, aromatic hydrocarbons, but the "outer" term is also somewhat larger, and these terms are of similar magnitude. The "outer" term is extremely sensitive to the "size" of the ion formed, and the rate of electron transfer in hydrazines would be predicted to be dominated by the "outer" electrostatic term if the theory were applied.

Both conformational change and electrostatic effects could be factors in lowering electron transfer rates in hydrazines, and experiments are under way to determine the relative importance of these factors.

Experimental Section

The synthesis of the compounds employed[4,7] and the ESR techniques used[4] have been previously described.

A Princeton Applied Research Model 170 instrument was used for the coulometric oxidations and CV experiments. The solvent employed was Burdick and Jackson Labs, Inc., acetonitrile or Aldrich Chemical Co., butyronitrile, 0.1 *M*, in tetrabutylammonium perchlorate.

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References and Notes

(1) S. F. Nelsen and J. M. Buschek, *J. Am. Chem. Soc.*, **96**, 6241 (1974).
(2) S. F. Nelsen and J. M. Buschek, *J. Am. Chem. Soc.*, **96**, 6987 (1974).
(3) S. F. Nelsen and P. J. Hintz, *J. Am. Chem. Soc.*, **94**, 7114 (1972).
(4) S. F. Nelsen, G. R. Weisman, P. J. Hintz, D. Olp, and M. R. Fahey, *J. Am. Chem. Soc.*, **96**, 2916 (1974).

(5) For a review of activation energies for conformational changes in amines and hydrazines, see J. M. Lehn, *Fortschr. Chem. Forsch.*, **15**, 311 (1970).
(6) (a) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964); (b) R. S. Nicholson, *ibid.*, **37**, 1351 (1965).
(7) S. F. Nelsen and P. J. Hintz, *J. Am. Chem. Soc.*, **94**, 7108 (1972).
(8) B. A. Kowert, L. Marcous, and A. J. Bard, *J. Am. Chem. Soc.*, **94**, 5638 (1972).
(9) (a) S. P. Sorensen and W. H. Bruning, *J. Am. Chem. Soc.*, **94**, 6352 (1972); (b) *ibid.*, **95**, 2445 (1973).
(10) F. Gerson and W. B. Martin, Jr., *J. Am. Chem. Soc.*, **91**, 1883 (1969), and references therein.
(11) J. E. Harriman and A. H. Maki, *J. Chem. Phys.*, **39**, 778 (1963).
(12) S. Terabe and R. Konaka, *J. Am. Chem. Soc.*, **95**, 4976 (1973).
(13) F. Gerson, B. Kowert, and B. M. Peake, *J. Am. Chem. Soc.*, **96**, 118 (1974), and references therein.
(14) R. A. Y. Jones, A. R. Katritzky, A. R. Martin, D. L. Ostercamp, A. C. Richards, and J. M. Sullivan, *J. Am. Chem. Soc.*, **96**, 576 (1974).
(15) S. F. Nelsen and P. J. Hintz, *J. Am. Chem. Soc.*, **93**, 7104 (1971).
(16) F. G. Riddell and P. Murray-Rust, *Chem. Commun.*, 1075 (1970).
(17) S. F. Nelsen and J. M. Buschek, *J. Am. Chem. Soc.*, **96**, 2392 (1974).
(18) S. F. Nelsen and J. M. Buschek, *J. Am. Chem. Soc.*, **96**, 7930 (1974).
(19) R. D. Allendoerfer and P. H. Rieger, *J. Am. Chem. Soc.*, **87**, 2236 (1965).
(20) (a) L. B. Anderson, J. F. Hansen, T. Kakihana, and L. A. Pacquette, *J. Am. Chem. Soc.*, **93**, 161 (1971); (b) L. B. Anderson and L. A. Paquette, *ibid.*, **94**, 4915 (1972).
(21) H. J. Heubert and D. E. Smith, *J. Electroanal. Chem.*, **31**, 333 (1971).
(22) L. A. Paquette, L. B. Anderson, J. F. Hansen, S. A. Lang, Jr., and H. Berk, *J. Am. Chem. Soc.*, **94**, 4907 (1972), and references therein.
(23) J. M. Fritsch, H. Weingarten, and J. D. Wilson, *J. Am. Chem. Soc.*, **92**, 4038 (1972).
(24) J. M. Hale in "Reactions of Molecules at Electrodes", N. S. Hush, Ed., Wiley-Interscience, New York, N.Y., 1971, Chapter 4, pp 229-258.

Kinetics and Mechanisms of the Loss of Water from the Cyclohexanol Radical Ion at Times from 50 Picoseconds to 10 Microseconds following Field Ionization

Peter J. Derrick,* John L. Holmes,[1] and Roger P. Morgan

Contribution from The Christopher Ingold Laboratories, University College,
University of London, London WC1H OAJ, United Kingdom.

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Abstract: The rates of loss of water from a series of specifically deuterated cyclohexanols have been measured at times as short as 50 psec following field ionization (FI) and at longer times extending to 10 μsec. It is concluded that FI does not induce ring cleavage in the molecular ion prior to water loss. A previously unidentified 1,2 elimination is the fastest process effecting loss of water; loss of water initiated by 1,4-hydrogen transfer is a slower process. It is suggested that, following electron impact (EI) at 70 eV, the more energetic molecular ions undergo rapid ring cleavage to form acyclic isomers, which may delay for up to microseconds before decomposing to eliminate water.

Cyclohexanol stands out as an archetypal reaction system in mass spectrometry. Friedel et al.[2] reported its electron impact (EI) mass spectrum in 1956 and drew attention to a major peak corresponding to loss of water from the molecular ion. By labeling specifically with deuterium, Djerassi et al.[3] found that approximately 40% of this $C_6H_{10}\cdot^+$ peak in the EI mass spectrum originated through elimination of the hydroxyl group and hydrogen from C-4, approximately 40% through elimination of the hydroxyl group and hydrogen from C-3 or C-5, and 10-20% through elimination of the oxygen atom together with two C-3 or C-5 hydrogens. The cis-4 hydrogen is lost to a greater degree than the trans counterpart,[4] supporting the proposal[5] that elimination is initiated by 1,4-hydrogen transfer across a boat-type structure of the intact cyclohexanol ion. Photoionization measurements[6] show that water is lost to a greater extent from *trans-tert*-butylcyclohexanol than from the cis epimer,[7] again in accord with 1,4 transfer within a boat form. Further support for this 1,4 transfer can be drawn from the EI mass spectra of cyclohexanediols.[5,8] The loss of the hydroxyl group and a hydrogen from C-3 or C-5 has been interpreted[3,5,9,10] as diaxial 1,3 elimination in a chair-type structure; analogous diaxial elimination has been suggested for water loss from hydroxy steroids.[11,12] More recently, Green et al.[13] have shown that, in the EI mass spectrum, the choice of hydrogen removed from C-3 is *not* stereospecific,[14] in contrast to the 80% cis-specific removal of hydrogen from C-4. Green et al.[13] interpret the lack of stereospecificity as evidence that the ring has opened prior to water loss involving these hydrogen atoms. The mechanism proposed by Djerassi et al.,[3] and supported by later work,[14] in which cyclohexanol isomerizes to the hexanal ion seems to account for water loss involving two hydrogens from C-3 and C-5. Ward and Williams[10] have reported EI metastable abundances for loss of water from specifically deuterated cyclohexanols and conclude that some degree of H/D randomization probably occurs prior to water elimination.[15] Holmes et al.[14] have also studied the EI metastable arising from water loss. They conclude that there is no H/D randomization preceding water loss from the ring-intact molecular ion but that, in the α-cleaved ion, there is some exchange between the hydroxyl and the C-2 and C-6 hydrogen atoms. These workers[14] suggest that the markedly reduced specificity[10,14] in the metastable region as compared with the normal mass spectrum arises because there is a greater abundance of ring-opened species among the longer lived ions.

We report novel kinetic data as to the loss of water from specifically deuterated cyclohexanols over a time range from 50 psec to 10 μsec following field ionization (FI). The essential feature of the method[16-18] employed, which is referred[18] to as "field ionisation kinetics (FIK)", is that decomposition of one charged molecule to another charged molecule occurs within a steep potential gradient (100 MV m^{-1}) so that the translational energy of the ionic fragment is dependent upon the position on the gradient at which decomposition occurred. The distribution of translational energy of the fragment ions is the quantity actually measured,