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

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Received December 4, 1974

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, and this defines the distribution of reactant lifetimes which can be calculated. One strong electric field both serves to produce the reactant radical ions by field ionization at a well-defined position (to within nanometers) and acts as the potential gradient within which decomposition occurs.[19] The shortest time intervals resolved to date are of the order of picoseconds. The field ionization (FI) process imparts a wide continuous distribution (perhaps extending over 100 kcal mol^{-1}) of excitation energy to the reactant radical ion, although the distribution appears to be highly asymmetric with a typical mean energy being in the vicinity of 10 kcal mol^{-1} (ref 20). Kinetic data over seven orders of magnitude of time are obtained, and Derrick et al.[18,21] have shown how this information can provide a strong basis for mechanistic inference.

Experimental Section

Measurements were made with a field ionization (FI) source designed and constructed at University College, which is described in detail elsewhere.[22] The source employs blade emitters, manufactured by the Schick Razor Blade Co., and has been designed for use with the commercial MS-9 double-focusing mass spectrometer. Measurements were made by focusing the mass spectrometer on the fragment ion of interest, and then scanning the potential on the blade.[22,23] These experimental curves of fragment ion current against blade potential represent the desired translational energy distribution broadened by an apparatus function.[17] We remove the instrumental broadening by approximating the apparatus function to a square function and correct the curves for the changes in total emission during the blade potential scan.[23] The transformation of translational energy to lifetime of the molecular ion is carried out according to standard principles[17,18,23] using conformal transformations and numerical integration to calculate ion trajectories.[24] These procedures yield the distribution of molecular ion lifetimes prior to decomposition to lose water over the range 50 psec to 1 nsec, and this distribution is synonymous with the dependence of the rate of decomposition upon time over this range.[17] Division of the rate of decomposition at a particular time by the total number of molecular ions remaining undecomposed at that time gives a rate constant, which we term a phenomenological rate constant $k(t)$.[18] This rate constant $k(t)$ is the probability relative to undecomposed reactant of a molecular ion decomposing to lose water at time t, under the particular conditions of the experiment, and is a function of time since the distribution of internal energy E over the assembly of molecular ions produced by FI is not Boltzmann. Current theories of chemical kinetics would define, what we term, a microscopic rate constant $k(E)$, which is the probability relative to undecomposed reactant of a molecular ion decomposing to lose water, given the ideal conditions in which all molecular ions possess the same discrete amount of internal energy E.[25] This rate constant $k(E)$ is predicted to be independent of time. The experimentally determined phenomenological rate constant $k(t)$ is related to the theoretical microscopic rate constant $k(E)$ by the expression:[18]

$$k(t) = \left[\int_0^\infty P(E)k(E)e^{-k(E)t}\mathrm{d}E\right] \Big/ \left[\int_0^\infty P(E)e^{-k(E)t}\mathrm{d}E\right] \qquad (1)$$

$P(E)$ is the distribution of internal energy E over the assembly of ions produced by FI. The relationship indicates how the phenomenological rate constant $k(t)$ could be regarded as a probability for decomposition averaged over all internal energies E.

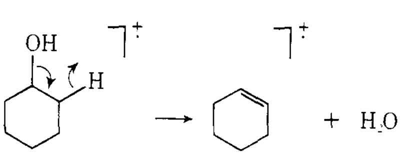
The data at times from 50 psec to 1 nsec are complemented by a data point at 30 nsec obtained from measurement of decomposition on the potential plateau between the focus electrodes in the source[23] and by two further data points at 700 nsec and 8 μsec obtained from measurement of the metastables in the first and second field-free regions of the mass spectrometer.[23]

The synthesis of the specifically deuterated cyclohexanols has been described.[14] Isotopic purities were estimated by low energy EI mass spectrometry to be as follows:

cis-cyclohexanol-*4-d_1*	94% d_1, 6% d_0
trans-4-d_1	10% d_2, 85% d_1, 5% d_0
4,4-d_2	92% d_2, 8% d_1
2,2,6,6-d_4	88% d_4, 3% d_3, 7% d_2, 2% d_1
3,3,5,5-d_4	90% d_4, 8% d_3, 2% d_2

Results and Discussion

Figure 1 shows phenomenological rate constants $k(t)$ for the loss of H_2O and HDO from cyclohexanol and its isotopic isomers *cis-4-d_1*, *trans-4-d_1*, *4,4-d_2*, *2,2,6,6-d_4*, and *3,3,5,5-d_4*. It is evident that, at times >1 nsec, the major loss of water (90% of decomposition) involves the cis-4 hydrogen. This high degree of specificity rules out the possibility of H/D randomization and strongly suggests that the cyclohexanol ring has remained intact with 1,4-hydrogen transfer occurring within a boat-type structure. The remaining 10% of water loss at these longer times appears to involve the *trans-4-d_1* to a small extent but must also involve hydrogens other than those at C-4 because the *4,4-d_2* species loses H_2O. Loss of HDO from the *2,2,6,6-d_4* or the *3,3,5,5-d_4* to the extent of a few percent (compared with loss of H_2O) could pass undetected because of the effects of isotopic impurities and the limits on the accuracy of the measurements at the longer times. The results with the *cis-4-d_1*, *trans-4-d_1*, and *4,4-d_2* species show that the bulk of water lost at the shortest time does not involve the 4-position. The only species to lose HDO at the shortest time is the *2,2,6,6-d_4* analog, there being no such loss from cyclohexanol-*3,3,5,5-d_4* at the shortest times. The $k(t)$-time curves for the *2,2,6,6-d_4* species can be integrated as in an earlier paper[26] to estimate the numbers of fragments formed between 50 psec and 1 μsec. The results as fractions of the total molecular ion current are 0.005 for m/e 85 (M − HDO) and 0.1 for m/e 86 (M − H_2O) giving a ratio (M − H_2O)/(M − HDO) of 20:1 (cf. 6:1 for 70-eV EI). The loss of deuterium from C-2 (and C-6) at the shortest times suggests 1,2 elimination from an intact ring to form the stable cyclohexene ion[27] (eq 2). The results for the *cis-4-d_1* and *4,4-d_2* species agree that the rate curves for the proposed 1,2 and 1,4 processes intersect at about 500 psec, whereas the results for the *2,2,6,6-d_4* species place the intersection at less than 100 psec. This difference probably reflects kinetic isotope effects. Beyond this, we hesitate to interpret quantitative differences *among the results for different molecules*. The results for the undeuterated and the *3,3,5,5-d_4* species, for example, are in poor agreement at the shortest times, and the reason is not clear. It must be borne in mind that the mechanism by which the energy content $P(E)$ imparted to a molecule by FI is not well understood and that, with the decomposition of cyclohexanol at very short times, only a very small fraction (a few percent) of the total number of molecular ions is involved.



(2)

The kinetics of the loss of water (Figure 1) are explained, if the proposed 1,2 elimination and the initial 1,4-hydrogen transfer compete with each other as the quasi-equilibrium theory would predict. The results for the overall loss of water via the 1,4 process may not, however, reflect only the rate of the 1,4-hydrogen transfer step since it is possible that an intermediate is involved. Certainly the steep rise in the rate constant over the interval 50 psec to 1 nsec is consistent with the intervention of an intermediate. Nevertheless it is clear that the 1,2 elimination does not occur to a significant extent at long times (μsec), which we attribute

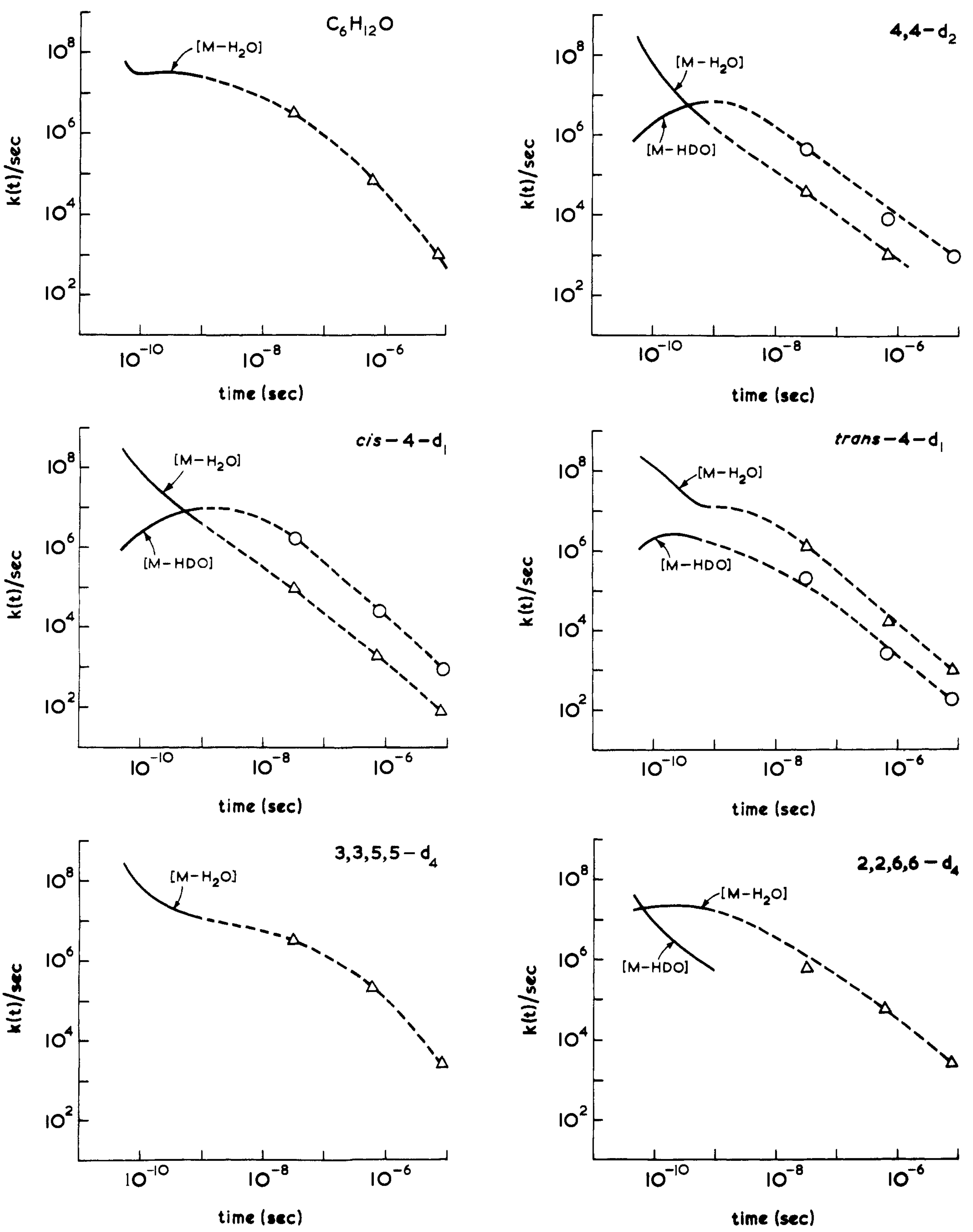


Figure 1. Phenomenological rate constants $k(t)$ as a function of time for the loss of water from cyclohexanol and a series of specifically deuterated analogs. The dashed lines are indicative of *interpolation* between the continua of data in the picosecond time frame and the isolated data points at longer times. The curves have been corrected to allow for isotopic impurities and for small contributions from a process effecting loss of water from protonated molecular ions $(M + 1)^+$. The statisticaal confidence limit in the rate constants is × 10%.

Table I. Relative Metastable Abundances for the Loss of H_2O, HDO, and D_2O from Specifically Deuterated Cyclohexanols in the First Field-Free Region following FI and EI at 70 eV

	FI			EI		
	H_2O	HDO	D_2O	H_2O	HDO	D_2O
cis-4-d_1	9	91		85	15	
trans-4-d_1	87	13		91	9	
4,4-d_2	8	92		71	29	
2,2,6,6-d_4	100			79	21	
3,3,5,5-d_4	100			40	44	16

to the process being suppressed by competition with 1,4 transfer due to the latter having a lower activation energy. The molecular ions decomposing at these times have relatively low average internal energies so that, in a competitive situation, it is the process with the lower activation energy which predominates.[21] A higher activation energy for the 1,2 process[28] may be rationalized on the grounds that the oxygen-C-2 hydrogen separation is large[29] (>2.3 Å in the neutral) and that the concerted elimination is "forbidden" by orbital symmetry for the ground electronic state. It is, however, clear that the 1,4-hydrogen transfer does not suppress 1,2 elimination at the short times (<1 nsec), which can be rationalized[21] on the grounds that the 1,4 transfer has a "tighter" transition state because of the need to confine the ring into the more rigid boat form. The situation in the cyclohexanol ion bears analogy to that in the hexanol ion, where water loss occurs via 1,3-hydrogen transfer at short times but via 1,4-hydrogen transfer at longer times.[30] The preference in the cyclohexanol ion for 1,2 to 1,3 transfer at short times may reflect a "tight" transition state for the latter due to restricting the ring in the chair form. 1,2 elimination of water occurs in the ethanol ion where competing processes are impossible.[31] Figure 2 shows microscopic rate constants $k(E)$ calculated by an approximate method on the basis that the 1,2 elimination has a higher activation energy and higher frequency factor ("looser" transition state) than the 1,4-hydrogen transfer; ring cleavage is discussed below.

Significance to Electron Impact

The EI mass spectra and metastable abundances of the deuterated cyclohexanols accord with those reported by Holmes et al.[14] Table I shows first field-free metastable abundances for the loss of water following EI and following FI. The observation of *significant* differences in the relative metastable abundances for decompositions of a particular molecular ion following FI and EI is to our knowledge unprecedented. We have measured metastables for the molecular ions of a number of aliphatic compounds and have observed *approximately* the same relative abundances for EI and FI in all cases except cyclohexanol.[22,32] The molecular ions undergoing metastable decomposition have similar lifetimes in EI and FI[33] so it might be expected that these two groups of reactive ions would have similar average internal energies and would decompose in like manner.[34] That this expectation is not fulfilled with cyclohexanol leaves two possible broad explanations. In either or both EI and FI, either internal energy is not randomized prior to decomposition in microseconds, or at least two processes effecting loss of water are not competing with each other in this time frame.[35]

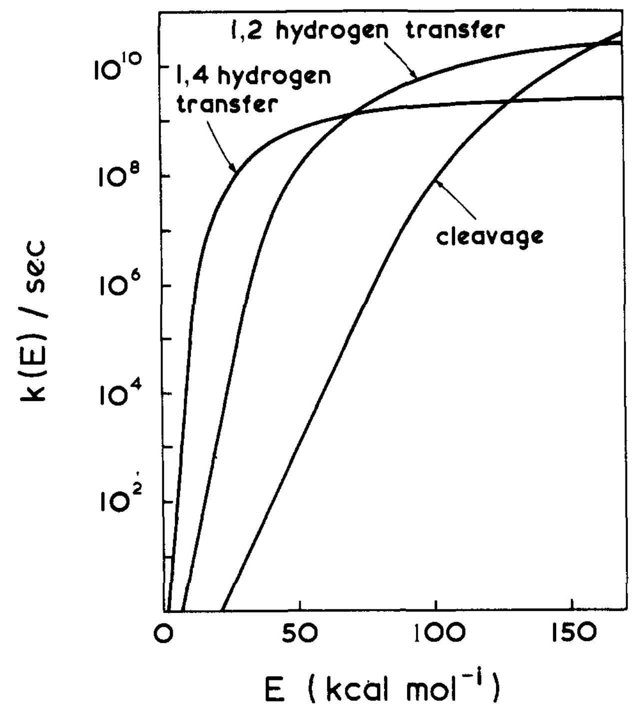


Figure 2. Calculated curves of microscopic rate constant $k(E)$ against internal energy E for 1,2- and 1,4-hydrogen transfer and for ring cleavage in the cyclohexanol ion. The curves describe only these elementary reactions and do not describe the overall loss of water; separate sets of curves are required for the further reactions of each of the proposed intermediates formed by 1,4-hydrogen transfer and ring cleavage. The curves were calculated from the expression $k(E) = \nu[(E - E_0)/E]^{s-1}$ provided by the quasi-equilibrium theory, interpolating at low energies where the expression is unreliable, between the activation energies E_0 and the calculated values ($>10^6$ sec^{-1}) of $k(E)$. In our choice of activation energies (2 kcal mol^{-1} for 1,4 transfer, 7 kcal mol^{-1} for 1,2 transfer, 22 kcal mol^{-1} for ring cleavage), we were guided by the appearance potentials (see later text) and the conclusions from our kinetic results. We set the frequency factors ν at 3×10^9 sec^{-1} for 1,4 transfer and 3×10^{13} sec^{-1} for ring cleavage, and varied that for the 1,2 transfer to obtain a value ($\nu = 2 \times 10^{11}$ sec^{-1}) which placed the intersections between the 1,2 and 1,4 curves and between the 1,2 and ring-cleavage curves in the regions suggested [$k(E) > 10^9$ sec^{-1} and $k(E) > 10^{10}$ sec^{-1}, respectively] by the experimental results (Figure 1) on the basis of expression I assuming a smooth distribution function $P(E)$ of the form calculated by Tenschert and Beckey.[20] A value of s equal to the total number of internal degrees of freedom ($s = 51$) has been assumed. We emphasize that the slopes of the curves are sensitive functions of this parameter, becoming steeper if the value of s is reduced.

That the cis- and trans-3 hydrogens are lost as water with equal probability both in the EI mass spectrum and as metastables indicates that these C-3 processes involve acyclic isomers of the cyclohexanol ion, and the general lack of stereospecifity manifested in the metastable decomposition following EI at 70 eV indicates that much [>90% (ref 14)] of this decomposition involves acyclic isomers;[13,14] whereas the stereospecificity of the metastable decomposition to lose water following FI indicates decomposition of a ring-intact cyclohexanol ion. The differing metastable abundances for EI and FI (Table I) could therefore be due to the participation of the acyclic isomers in the former case but not in the latter. If we accept this explanation as being basically correct, the question remains of why cyclohexanol ions formed by FI do not undergo ring cleavage. We suggest that only cyclohexanol ions with high internal energies, accessible by EI at 70 eV but not by FI, undergo ring cleavage and that, although the ring cleavage is rapid (see Figure 2), subsequent decomposition to lose water is sufficiently slow to contribute to the metastables. This slow decomposition, we suggest, is due to energy being required to cleave the ring so that the acyclic species possess significantly less vibrational energy than the cyclic precursor.

We sought to evaluate our interpretation of the kinetic results[36] by measuring EI appearance potentials for the loss of water from the deuterated cyclohexanols, using the EI source of the MS-9 and the semilog method[37] in which the logarithm of the fragment ion current, expressed as the fraction of its value at 50 eV, is plotted against electron energy. The ionization potential of cyclohexanol and the appearance potential of m/e 82 [M − H_2O] were found to be 10.0 ± 0.2 and 10.2 ± 0.2 eV, respectively, which compare with the respective values of 9.63 and ≤9.80 eV determined by Lossing[38] with energy-resolved electron beams. The appearance potentials of m/e 86 [M − H_2O] and 85 [M − HDO] from cyclohexanol-*3,3,5,5*-d_4 were found to be 10.2 ± 0.2 and 10.7 ± 0.2 eV, respectively. The semilog plots for m/e 84 [M − H_2O] and 83 [M − HDO] from the cyclohexanol-*4,4*-d_2 were only approximately parallel to each other; however, it was clear that the appearance potentials were similar (to within 0.4 eV). The semilog plots for m/e 86 [M − H_2O] and 85 [M − HDO] from cyclohexanol-*2,2,6,6*-d_4 crossed over each other at about 1 eV; however, it was again clear that the appearance potentials were similar. According to our proposals, m/e 86 [M − H_2O] from cyclohexanol-*3,3,5,5*-d_4 is formed from the ring-intact cyclohexanol ion by the low-energy 1,2 and 1,4 processes, and probably also via acyclic isomers to some extent, whereas m/e 85 [M − HDO] is formed by decompositions initiated by the high-energy ring cleavage of the cyclohexanol ion. That the appearance potential of m/e 85 [M − HDO] is 0.5 eV higher than that of m/e 86 [M − H_2O] is therefore consistent with our interpretation. The m/e 86 [M − H_2O] from cyclohexanol-*4,4*-d_2 is formed both from the ring-intact ion by the 1,2 process and from the acyclic isomers, and m/e 85 [M − HDO] from the ring-intact ion by the 1,4 process, and probably from the acyclic isomers to some extent as well. That the appearance potentials of these ions are similar suggests that the activation energies for the 1,4 and 1,2 processes do not differ by more than an estimated 10 kcal mol^{-1}; the calculations (Figure 2) show that a difference of 5 kcal mol^{-1} in the activation energies for the 1,4 and 1,2 processes adequately explains the kinetic results. The appearance potentials for cyclohexanol-*2,2,6,6*-d_4 are similarly consistent with the interpretation of the kinetic results.

Conclusion

Following FI, water is eliminated from the ring-intact cyclohexanol ion by a fast 1,2-elimination process and by a slower process initiated by transfer to the oxygen of the cis-4 hydrogen; 1,3-hydrogen transfer is not a significant process in the ring-intact ion. The differing relative metastable abundances following EI and FI for loss of H_2O, HDO, and D_2O from specifically deuterated cyclohexanols are attributed to the participation of acyclic $C_6H_{12}O^{\cdot +}$ species in the case of EI but not with FI.

Acknowledgments. We express our gratitude to the Ramsay Memorial Fellowships Trust for the award (to P.J.D.) of the General Fellowship (1973-1975) and to the Science Research Council (U.K.) for a maintenance grant (to R.P.M.). We gratefully acknowledge the financial support of the Central Research Fund (University of London) in setting up the apparatus. We gratefully acknowledge Schick Safety Razor Co. to whom we are indebted for the generous gift of the razor blades used in our experiments. We thank Dr. M. A. Baldwin for assistance with appearance potential measurements on the GEC-AEI MS-9 and Dr. R. T. B. Rye for synthesizing samples of certain labeled cyclohexanols. We acknowledge valuable discussion with Dr. M. A. Baldwin, Dr. A. G. Loudon, and Professor A. Maccoll. We are particularly grateful to Dr. F. P. Lossing for kindly measuring a number of appearance potentials using energy-resolved electron beams and for his expert advice on the interpretation of our appearance potential measurements.

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(25) It is implicitly assumed that internal energy E is randomly distributed among all vibronic states of the molecular ion, and that intermediates are not involved in the decomposition. If intermediates are involved, the *overall decomposition* must be treated as a *series* of consecutive reactions, each of which is described by a separate rate constant $k(E)$.

(26) P. J. Derrick, A. M. Falick, and A. L. Burlingame, *J. Am. Chem. Soc.*, **94**, 6794 (1972).

(27) The kinetics of the loss of HDO from cyclohexanol-*2,2,6,6*-d_4 (Figure 1) would be consistent with simple bond cleavage; however, the possibility that the molecular ion loses a hydroxyl radical and a hydrogen atom rather than water must be ruled out because of energetic considerations. Summing the heats of formation[38] of the cyclohexene ion, the hydroxyl radical, and the hydrogen atom shows that the energy required to form these species from the cyclohexanol ion is >112 kcal mol^{-1}; appearance potentials (see later text) show that the activation energy for the lowest energy process effecting loss of water from the cyclohexanol ion is <4 kcal mol^{-1} and that the activation energy for loss of HDO from the cyclohexanol-*2,2,6,6*-d_4 ion is low (<20 kcal mol^{-1}). Calculation using the simplest expression provided by the quasi-equilibrium theory (see caption for Figure 2) indicates that, for the successive loss of hydroxyl radical and hydrogen atom to occur in less than a nanosecond, the cyclohexanol ion must have internal energy of several hundred kilocalories per mole. Internal energies of this magnitude are not expected to be produced by FI in our experiments, and this expectation is confirmed by the absence of the fragment ions from the high energy decomposition processes (e.g., α cleavage and formation of m/e 57) characterized in earlier studies[10,14,15] using EI at 70 eV.

(28) Since the 1,2 elimination is exothermic (by 9 kcal mol^{-1}) according to the determined heats of formation,[38] the activation energy would indicate that there is an energy hump, and hence a reverse activation energy, along the reaction pathway.

(29) C. C. Fenselau and C. H. Robinson, *J. Am. Chem. Soc.*, **93**, 3070 (1971).

(30) P. J. Derrick, A. M. Falick, and A. L. Burlingame, *J. Am. Chem. Soc.*, **95**, 437 (1973).

(31) J. Momigny, *Bull. Soc. R. Sci. Liege*, **24**, 111 (1955).

(32) (a) P. J. Derrick and A. G. Loudon, unpublished results; (b) R. P. Morgan

and P. J. Derrick, *Org. Mass Spectrom.*, in press.

(33) The time-window for metastable decomposition in the first field-free region extends to shorter times (10^{-7} sec) with FI than with EI. However, the differences in metastable abundances are not due to the wider time-window since the same differences between FI and EI are observed with the second field-free metastables for which the time-windows with FI and EI are more similar to each other.

(34) For an excellent discussion of the relevant aspects of unimolecular reaction theory, see W. Forst, "Theory of Unimolecular Reactions", Academic Press, New York, N.Y. 1973.

(35) These two statements are to some extent synonymous. Decomposition of isolated electronic states do not compete, and internal energy is not randomized over all vibronic states; whereas decompositions of noninterconverting isomeric structures also do not compete, but this is generally not regarded as a failure to achieve energy randomization.

(36) Metastable intensities at electron energies below nominal 12 eV were too low for meaningful measurement. We confirmed, however, the report of Green et al.[13] that loss of water involving the cis-4 hydrogen does rise in importance in the EI mass spectrum relative to processes involving C-3 (C-5) hydrogens as the electron energy is taken below 20 eV.

(37) M. A. Baldwin, A. Kirkien-Konasiewicz, A. Maccoll, and B. Saville, *Chem. Ind.* (*London*), 286 (1966).

(38) F. P. Lossing, private communication, 1974.

Rotational Deactivation, Energy Localization, and Reactivity in the Photochemistry of 1-Methylene-4-phenyl-4-vinylcyclohex-2-ene

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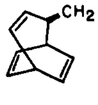
Received January 2, 1975

Abstract: The singlet and triplet photochemistry of 1-methylene-4-phenyl-4-vinylcyclohex-2-ene (**5**) has been studied. Triplet sensitized irradiation of **5** gives exclusively vinyl migration to produce *trans*-1-methylene-5-phenyl-6-vinylbicyclo[3.1.0] hexane (**13**) in good yield (83%) but low efficiency [$\Phi = 0.006$]. However, direct excitation of **5** at 253.7 nm affords phenyl migration yielding *trans*-1-methylene-6-phenyl-5-vinylbicyclo[3.1.0]hexane ($\Phi = 0.08$). The contrasting products from direct and sensitized irradiation are attributed to energy localization in the singlet and triplet states of the molecule. The observation of triplet reactivity in an exocyclic methylene system such as **5** is discussed with reference to the concept of rotational deactivation of excited states.

The establishment of the general structural factors which influence excited state reactivity is one of the prime goals of organic photochemistry. One such factor is the alteration of reactivity arising from geometric change about atoms having much lower bond orders in the excited state vs. the ground state. To date rotational deactivation effects[2] have important consequences on the multiplicity and reactivity of di-π-methane[3] and oxa-di-π-methane[4] systems, of olefins in photoaddition processes,[5] and of photocycloaddition processes of enones[6] and imines.[7] The presence of rotational deactivation may likewise contribute to the low emission yields of many acyclic olefin systems.[8]

Since our initial work in establishing the importance of rotational deactivation in the di-π-methane system,[3a] several compounds have been reported which still undergo this rearrangement despite the presence of a potential rotational deactivation process.[3c] In view of the general significance of rotational freedom in altering excited state reactivity, we were interested in establishing those structural features of a molecule which permit efficient triplet reactivity even when rotational deactivation mechanisms can be operative. Especially interesting were molecules such as **1**[9] and **2**[10] which had been reported to undergo efficient triplet di-π-methane rearrangements. These two systems are in marked contrast to the acyclic diene-phenyl system **3**[11] and the diphenyl system **4**[12] which show very low triplet di-π-methane reactivity. Two structural features differ in these two sets of compounds. First, for compounds **1** and **2** the initial bridging process could involve bonding between two olefinic moieties,[13] while for **3** and **4** diene-phenyl bonding would be necessarily involved in the initial phase of the reaction. Since the former would reasonably correspond to a lower energy situation, the dichotomy would then be explained by a more facile bridging process in **1** and **2** vs. **3** and **4**. Second, in molecules such as **1** and **2**, the extensive π interaction in the excited state forced by the rigid bicyclic system could seriously alter the energetics of twisting about the exocyclic methylene group. Thus, in these systems rotational deactivation could be less effective than in compounds **3** and **4**.



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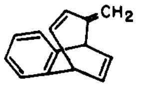

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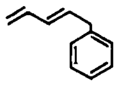

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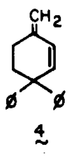

4

A system which we felt would focus attention on this problem was 1-methylene-4-phenyl-4-vinylcyclohex-2-ene (**5**). This molecule would possess the low energy diene-olefin interaction of **1** and **2**, yet the potentially strong bicyclic conjugation present in the excited state of these molecules would be absent. We wish to present here a study of the singlet and triplet photochemistry of **5**.

Synthesis of 1-Methylene-4-phenyl-4-vinylcyclohex-2-ene (5). The synthesis of **5** began with the known 2-carbomethoxy-4-cyano-4-phenylcyclohexane[14] (**6**) and is outlined in Scheme I. The steps, except for the formation of **12** from **11**, proceeded smoothly and reproducibly. However, yields for the **11** → **12** sequence were somewhat variable (20-50%); in addition, **12** was contaminated with 5-20% of the difficultly separable **11**.[15]

Sensitized Irradiation of 5. Preparative sensitized irradiation of **5** using 2-acetonaphthone (E_T = 59.5 kcal mol^{-1}) as sensitizer at 3500 Å resulted in disappearance of **5** and formation of one product in 83% yield. The photoproduct was separated from the sensitizer by silica gel chromatography and was shown to be isomeric with starting material by mass spectral and combustion analyses. By analogy with