

FIELD IONIZATION KINETICS OF THE LOSS OF H₂O FROM STEREOISOMERIC CYCLOHEXANEDIOL RADICAL IONS *

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ABSTRACT

The loss of H₂O from the molecular ions of *trans*- and *cis*-cyclohexane-1,2-diol (1a, b), *trans*- and *cis*-cyclohexane-1,3-diol (2a, b) and *trans*- and *cis*-cyclohexane-1,4-diol (3a, b) following field ionization has been measured at reaction times between $\sim 1 \times 10^{-11}$ and 1×10^{-9} s. The loss of H₂O from the molecular ions of 1a and 1b is not an important process and shows no differences between the stereoisomers. The curves of the normalized rate constant $k(t)$ versus reaction time τ for the *cis* stereoisomers 2b and 3b indicate a set of competing mechanisms for H₂O elimination from these ions, in analogy to the corresponding fragmentation of cyclohexanol ions. By contrast, $k(t)$ is much larger at short τ and increases to a distinct maximum at $\tau_{\max} = 1.1 \times 10^{-10}$ s in the case of the *trans* isomers 2a and 3a. By using specifically deuterated derivatives, it is shown that these differences are due to the occurrence of additional elimination processes corresponding to activated transannular 1,3- and 1,4-elimination of H₂O, respectively. The important effects of the conformations and conformational changes of the molecular ions on these fast unimolecular reactions are discussed.

INTRODUCTION

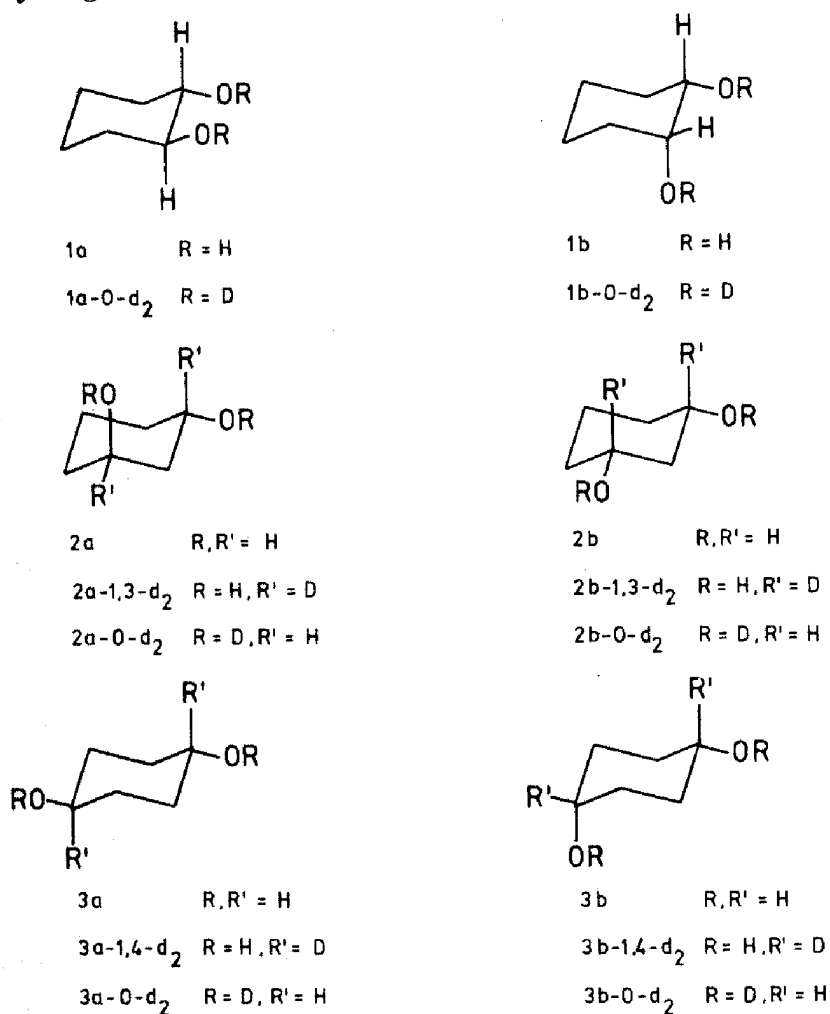
The observation by Beckey et al. [1] that the unimolecular decomposition of organic ions travelling through the accelerating field of an ion source after field ionization (FI) can be detected and followed on a time scale of some picoseconds to microseconds has initiated the development of the method of field ionization kinetics (FIK) [2]. By this elegant technique the fast unimolecular reactions of ions can be studied and some interesting details of the reaction mechanisms emerging from investigations using the time-integrating methods of conventional mass spectrometry can be resolved. This detailed view of the reaction can reveal very subtle effects of ion structure on reaction rates, and as the FIK technique can be performed with the normal

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equipment of a mass-spectrometric analytical laboratory this may be important for analytical applications.

FIK studies of the isomerization and rearrangement reactions of organic molecular ions have shown [2,3] that a multitude of reactions occur and are nearly complete within a few nanoseconds after ion formation. It is also apparent from these studies that the fast fragmentations of energetically excited ions approach the time frame of changes in the conformation of an organic molecule by internal rotations. Hence FIK studies are of interest for certain reactions of ions from stereoisomeric compounds, which have to undergo different conformational movements to adopt the conformation of the critical complex of that fragmentation (the "reactive conformation").

Differences in the electron impact (EI) and chemical ionization (CI) mass spectra of stereoisomeric compounds are well known [4]. Especially clear cases are the mass spectra of stereoisomeric cyclic diols and their derivatives [5] and of the related phenyl-substituted cyclanols [6]. The molecular ions of alkanols eliminate H_2O with a small activation energy via an internal hydrogen-atom abstraction by the ionized hydroxy group. In the stereoiso-



Scheme 1

mers mentioned above, one of the hydrogen atoms is predisposed to this hydrogen transfer because of a low dissociation energy. However, whether or not this predisposed hydrogen atom can approach the hydroxy group in the reactive conformation for H_2O elimination depends on the geometry of the stereoisomer and its conformational flexibility. Indeed, it has been shown by EI mass spectrometry that molecular ions do change their conformation before fragmentation, similarly to the neutral molecules, and that these changes affect ion intensities in the mass spectra [7]. In a recent FIK investigation of H_2O loss from ions of stereoisomeric decalin-1,4-diols [8], FIK curves with distinct maxima and minima were observed. By the use of specifically deuterated derivatives it has been shown that these variations of the rate constant for complete H_2O elimination with the lifetime of the ions are due to different elimination reactions, which reach their maximum rate constants [9] at different ion-lifetimes depending upon the molecular geometry and flexibility. Decalindiols are rather rigid molecules and, starting from the normal conformation, cooperative rotation about quite a number of C—C bonds is necessary for the molecular ions to reach the reactive conformations for H_2O elimination reactions other than 1,2-elimination. In this paper the results of a FIK study of H_2O elimination from the molecular ions of the stereoisomeric cyclohexanediols 1–3 (Scheme 1) are presented.

EXPERIMENTAL

The FI mass spectra and the FIK measurements were obtained using a Varian MAT 311A mass spectrometer equipped with an FI/EI source as described elsewhere [8], using wire emitters (tungsten, 10- μm diameter) activated with benzonitrile. For FIK measurements the ion-source lenses were kept at earth potential. All measurements were made with the same FI emitter under identical experimental conditions. The FIK curves obtained were corrected for the variation of the molecular ion intensities with the emitter potential and the integration time Δt of the method. The curves shown in the figures are the means of at least three independent measurements. The reproducibility is >90%. For the curves of $k(t)$ versus τ for the deuterated derivatives, the values of $k(t)$ have been corrected for ^{13}C contributions.

Trans-cyclohexane-1,2-diol (1a) [10] and cis-cyclohexane-1,2-diol (1b) [11] were prepared by methods given in the literature. Trans-cyclohexane-1,3-diol (2a) and cis-cyclohexane-1,3-diol (2b) were obtained by separation of the commercially available mixture of the stereoisomers by fractional distillation of the boranates [12]. Similarly, trans-cyclohexane-1,4-diol (3a) and cis-cyclohexane-1,4-diol (3b) were prepared by fractional crystallization of the diacetates [13] from the mixture of the stereoisomers.

Trans- and cis-cyclohexane-1,3-diol-1,3- d_2 (2a, b-1,3- d_2) were synthesized from cyclohex-2-enone-3- d_1 (from 3-ethoxycyclohex-2-enone and LiAlD_4

at 20°) by reduction with LiAlD_4 at -10°C , oxymercuration of the resulting cyclohex-2-enol-1,3- d_2 , and separation of the mixture of stereoisomers as described before. *Trans- and cis-cyclohexane-1,4-diol-1,4- d_2* (**3a**, **b-1,4- d_2**) were obtained from cyclohexane-1,4-dione by reduction with LiAlD_4 and separation of the stereoisomers. The d_2 -substitution of **2a**, **b-1,3- d_2** and **3a**, **b-1,4- d_2** was greater than 97% (by mass spectrometry). The *O-deuterated derivatives* of the cyclohexanediols were prepared by repeated exchange with D_2O and conditioning of the mass spectrometer with D_2O shortly before measurement. In spite of this, the H/D exchange was incomplete and some back-exchange occurred during the measurements (see also Table 2).

The purity of the stereoisomers as tested by gas chromatography (GC column OV-17 and Carbowax 4000) of the corresponding bistrifluoroacetate and bis-TMS ethers was better than 98% for all compounds.

RESULTS AND DISCUSSION

The FI mass spectra of the isomeric cyclohexanediols **1a**, **b-3a**, **b**, obtained using an activated-wire emitter under usual FI conditions, contain only a few signals besides those of the $\text{M}^{+\cdot}$ ion at m/z 116 and the $[\text{M} - \text{H}_2\text{O}]^{+\cdot}$ ion at m/z 98 (Table 1), and which arise from the latter ions by loss of H and H_2 . No cluster ions $(\text{M})_n^+$ were observed at the ion-source temperatures used ($\sim 270^\circ\text{C}$).

The FI spectra of *trans*-cyclohexane-1,2-diol (**1a**) and its *cis* stereoisomer **1b** differ only slightly in the relative abundances of ions $[\text{M} - \text{H}]^+$ and $[\text{M} - \text{H}_2\text{O} - \text{H}_2]^{+\cdot}$ but are identical with respect to loss of H_2O from the molecular ions. In contrast, the FI mass spectra of *trans*-cyclohexane-1,4-diol (**3a**) and *cis*-cyclohexane-1,4-diol (**3b**) show distinct differences in the relative abundances of $[\text{M} - \text{H}_2\text{O}]^{+\cdot}$ ions, the fragmentation being favoured

TABLE 1

FI mass spectra of cyclohexanediols **1a**, **b-3a**, **b** and the corresponding $k(t)_{\text{max}}$ and τ_{max} in the FIK curves

m/z	1a	1b	2a	2b	3a	3b
117	7.5	7.5	6.5	17.5	7.5	7.5
116	100	100	85	100	100	100
115	<0.5	3.0	2.0	3.0	6.0	1.0
114	—	2.0	8.0	1.0	8.0	2.0
99	<0.5	<0.5	7.0	<0.5	3.5	<0.5
98	2.0	2.5	100	2.0	14.0	2.5
97	—	—	—	1.5	—	1.0
96	<0.5	1.0	9.0	2.5	7.0	4.0
$k(t)_{\text{max}}(10^8 \text{ s}^{-1})$	—	—	600	31	200	8.4
$\tau_{\text{max}}(10^{-10} \text{ s})$	—	—	1.2	1.6	1.15	1.35

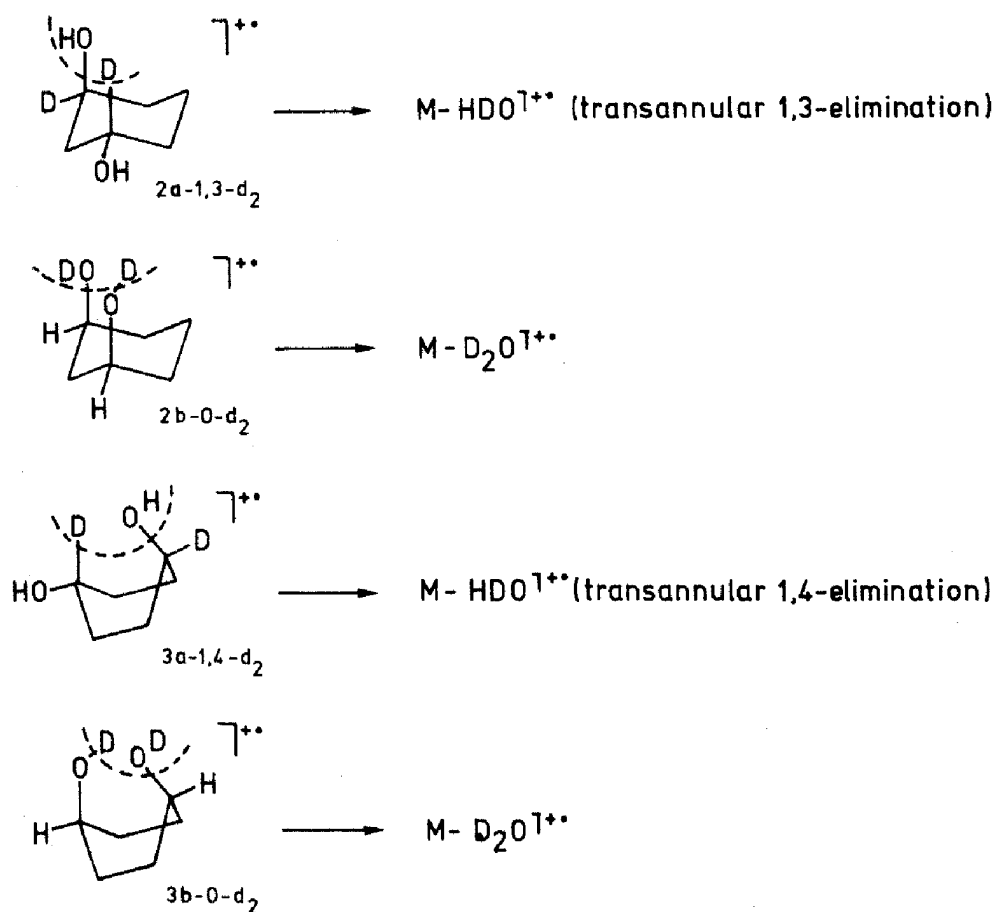
TABLE 2
 FI mass spectra of some specifically deuterated cyclohexanediols

<i>m/z</i>	1a-O-d₂	1b-O-d₂	2a-O-d₂	2a-1,3-d₂	2b-O-d₂	3a-O-d₂	3a-1,4-d₂	3b-O-d₂	3b-1,4-d₂
119	8	8	9	7	9	7	6	7	8
118	100	100	100	100	100	100	100	100	100
117	38	15	15	3	13	13	2	17	1
116	7	2	5	4	4	2	3	3	1
115	—	—	2	2	3	8	8	2	2
100	<1	<1	4	9	—	<1	2	<1	2
99	1	<1	100	100	<1	11	10	<1	<1
98	3	2	9	4	2	3	1	2	3
97	—	—	—	8	5	2	8	<1	—
96	—	—	10	—	3	9	—	4	—

for the *trans* derivative 3a by a factor of 6. The differences in the FI mass spectra of *trans*-cyclohexane-1,3-diol (2a) and *cis*-cyclohexane-1,3-diol (2b) are even larger. While the FI mass spectrum of the *cis* stereoisomer 2b is similar to those of the other *cis*-diols 1b and 3b with respect to the low intensity of $[M - H_2O]^{+}$ ions, these ions give rise to a base peak in the FI mass spectrum of the *trans*-diol 2a corresponding to an enhancement of H_2O elimination by a factor >50 compared to 2b.

The FI mass spectra of the deuterated cyclohexanediols, labelled at the carbinol carbon atoms (2a, b-1,3- d_2 ; 3a, b-1,4- d_2 ; see Scheme 1) or at the hydroxy groups (1a, b- $O-d_2$; 2a, b- $O-d_2$; 3a, b- $O-d_2$; see Scheme 1), respectively, reveal that the differences in the FI mass spectra reflect differences in the reaction mechanism of H_2O elimination even at very short lifetimes of the molecular ions (Table 2).

The strongly preferred elimination of HDO from the labelled *trans* derivatives 2a-1,3- d_2 and 3a-1,4- d_2 indicates transannular 1,3- and 1,4-elimination, respectively (Scheme 2). The course of H_2O elimination from the other deuterated molecular ions at short reaction times τ is less clear, because of the low intensities of the fragment ions and incomplete labelling in the case of the $O-d_2$ derivatives. However, the loss of D_2O from 1a- and 1b- $O-d_2$, which



Scheme 2

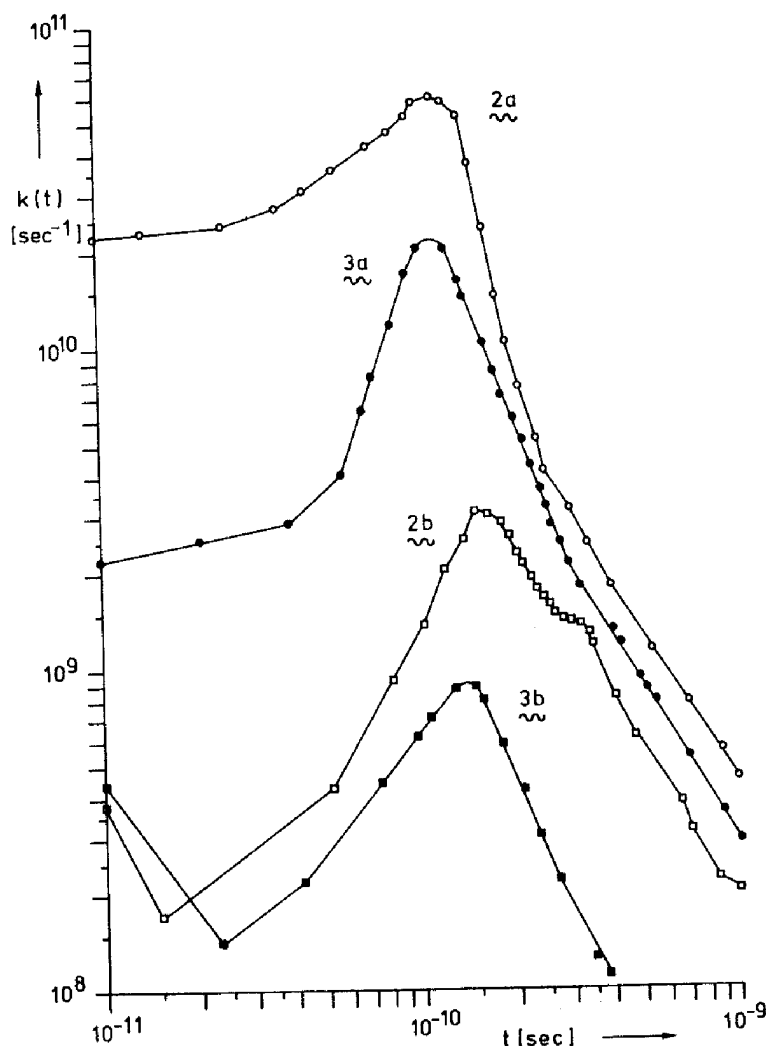


Fig. 1. Normalized rate constants $k(t)$ as a function of reaction time τ for the complete loss of H_2O from the molecular ions of 2a, 2b, 3a and 3b.

have the same relative orientation of the vicinal hydroxy groups in their molecular ions, shows that elimination by a reaction between both OD groups predominates. Similarly, predominant loss of D_2O is observed from the molecular ions of 2b- and 3b- O-d_2 , indicating again a transannular reaction between both OD groups during the elimination (Scheme 2).

The course of H_2O elimination from the molecular ions of the isomeric cyclohexanediols as shown by the FI mass spectra of the specifically deuterated derivatives agrees well with the results obtained by EI mass spectrometry [5]. From this congruence between the reactions at short lifetimes (FI) and during an integrated time up to microseconds (EI) it is expected that the specific mechanisms of H_2O elimination will prevail at all reaction times. This is corroborated by the results of the FIK measurements.

Figure 1 shows the variations with ion lifetime of the normalized rate con-

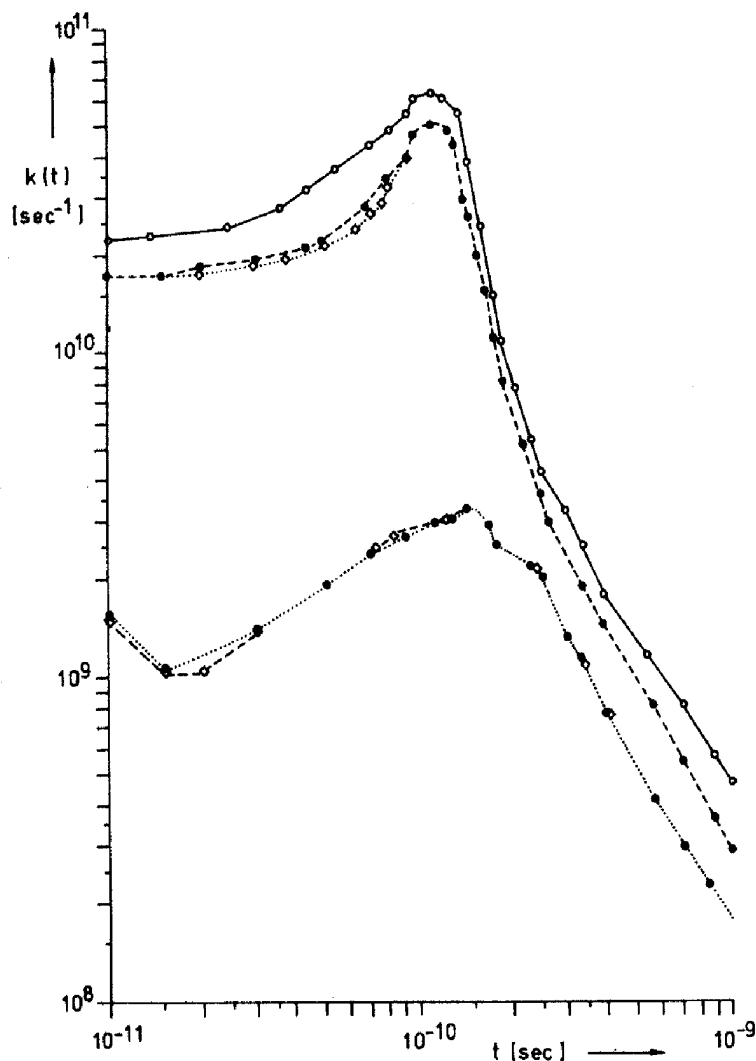


Fig. 2. Normalized rate constants $k(t)$ as a function of reaction time τ for the loss of H_2O from *trans*-cyclohexane-1,3-diol (2a) (\circ — \circ), loss of HDO (\bullet — \bullet) and H_2O (\bullet ···· \bullet) from 2a-1,3- d_2 , and loss of HDO (\diamond ···· \diamond) and D_2O (\diamond — \diamond) from 2a-O- d_2 .

stants [9] $k(t)$ for overall H_2O elimination, for the stereoisomers 2a, b and 3a, b. The FIK curves for loss of H_2O from 1a, b have been omitted, because $k(t)$ for both stereoisomers drops quickly and uniformly from a low starting value to very small values. H_2O elimination from these molecular ions is obviously a reaction with a rather large activation energy and not influenced by any conformational changes. The FIK curves for the other cyclohexanediols show more structure and exhibit maxima within a small range of reaction times τ (Table 1). The differences between the stereoisomers 2a and 2b, and 3a and 3b, respectively, are retained at all values of τ . The ratio of the normalized rate constants $k(t)_{\text{max}}$ at τ_{max} is 19.4 for 2a/2b and 23.8 for 3a/3b, i.e., in both sets of stereoisomeric cyclohexanediols the rate of elimination of H_2O from the *trans* isomer is enhanced by a factor of 20.

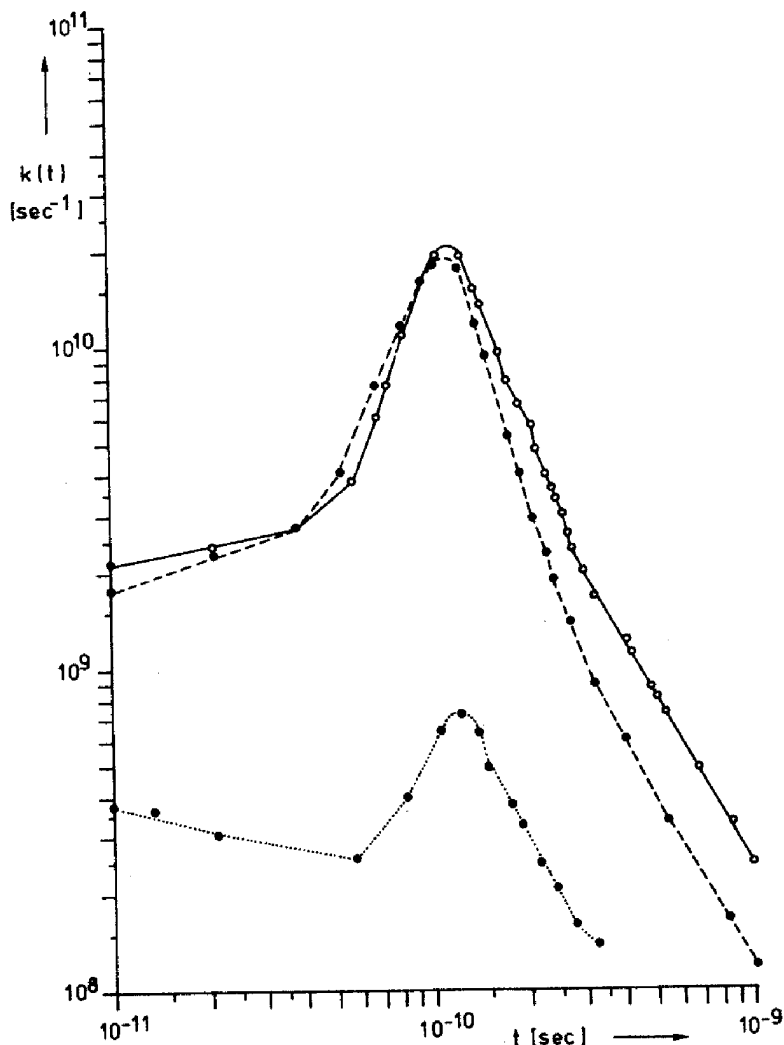


Fig. 3. Normalized rate constants $k(t)$ as a function of reaction time τ for the loss of H_2O from *trans*-cyclohexane-1,4-diol (3a) (○—○), and loss of HDO (●—●) and H_2O (●...●) from 3a-1,4- d_2 (the curves for loss of HDO and D_2O from 3a- $O-d_2$ are identical with those for loss of HDO and H_2O , respectively, from 3a-1,4- d_2).

In contrast to decalin-1,4-diols [8], which show maxima (and minima) in the FIK curves for complete H_2O elimination because of an overlap in time of different reaction mechanisms, the FIK curves at least in the case of the *trans*-diols 2a and 3a are determined by a single mechanism for loss of H_2O independent of τ . In Figs. 2 and 3 the results of FIK measurements of the losses of H_2O , HDO and D_2O from the labelled derivatives of 2a and 3a are compared with the overall losses of H_2O from the unlabelled diols. Neglecting isotope effects, 70–80% of the total loss of H_2O from the molecular ion of *trans*-cyclohexane-1,3-diol (2a) corresponds to a 1,3-transannular elimination throughout the span of τ -values investigated. It is difficult to decide which mechanisms are responsible for the remaining H_2O losses, because of the low ion intensities and incomplete labelling, but the normal-

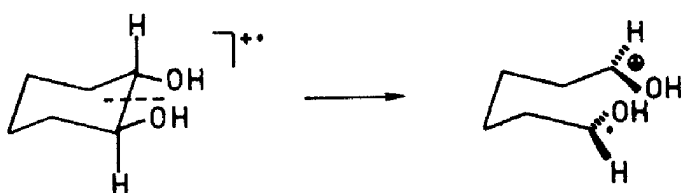
ized rate constants $k(t)$ for the elimination of H_2O from $2a\text{-}1,3\text{-}d_2$ and of D_2O from $2a\text{-}O\text{-}d_2$ are similar, both in magnitude and their dependence on τ , to $k(t)$ for the complete loss of H_2O from the *cis* isomer $2b$ (and for the loss of D_2O from $2b\text{-}O\text{-}d_2$). Since the loss of D_2O from $2a\text{-}O\text{-}d_2$ ions is only possible after initial cleavage of the cyclohexane ring, the minor part of H_2O elimination from $2a$ and the loss of H_2O from $2b$ are very likely due to a mixture of reaction mechanisms, which at the present time cannot be resolved with any certainty.

Similarly, from a small τ until τ_{max} , >90% of the loss of H_2O from $3a$ ions corresponds to transannular 1,4-elimination (Scheme 2), and subsequently the percentage of ions participating in this reaction drops to 50% at larger τ -values. Again, the remainder of the $3a$ ions react with $k(t)$ similar in magnitude and variation with τ to that for the molecular ions of the *cis* isomer $3b$.

Derrick et al. [14] have investigated the kinetics of the loss of H_2O from cyclohexanol ions using the FIK technique. They identified 1,2-elimination of H_2O as the fastest process with $k(t) \approx 5 \times 10^8 \text{ s}^{-1}$ at reaction times $\tau < 10^{-10} \text{ s}$, decreasing uniformly towards longer reaction times, and transannular 1,4-elimination reaching its maximum $k(t) \approx 10^7 \text{ s}^{-1}$ between $\tau = 10^{-10}$ and 10^{-9} s . The differences (and similarities) of the kinetics of the loss of H_2O from cyclohexanol ions and from the molecular ions of the cyclohexanediols 1–3 can be understood by taking into account:

- (i) differences in the activation energies of the various H_2O elimination reactions, especially those involving activated C–H bonds [15]; and
- (ii) entropic effects due to the different conformational requirements of the elimination reactions.

The curves of $k(t)$ versus reaction time τ for the loss of H_2O from the molecular ions of cyclohexanol [14] and from the *cis*-diols $2b$ and $3b$ (see Fig. 1) are similar; the differences may be due to the different reaction conditions and may be within the reproducibility of the method. The initial decrease of $k(t)$ for $2b$ and $3b$ can be attributed to 1,2-elimination of H_2O , as observed for cyclohexanol ions [14], and similarly the subsequent increase of $k(t)$ indicates an increasing importance of other elimination mechanisms, observed also for cyclohexanol. One expects therefore a large initial value of $k(t)$ for both the stereoisomeric cyclohexane-1,2-diols $1a$ and $1b$ and preponderance of the 1,2-elimination mechanism at all τ because a hydrogen atom at a carbinol group with a reduced C–H bond-dissociation energy [16] can participate in this process, lowering its activation energy. However, this is not observed, $k(t)$ for the loss of H_2O from $1a, b$ being small at short τ and even smaller at longer τ . The different behaviour of $1a, b$ compared to cyclohexanol and the other diols can be explained by a fast cleavage of the C1–C2 bond in the molecular ion preceding the loss of water (Scheme 3), in agreement with the results of EI mass spectrometry of these compounds [5]. The participation of some ring-opened molecular ions in the H_2O elimination reaction is also indicated for $2a, b$ and $3a, b$ by the results



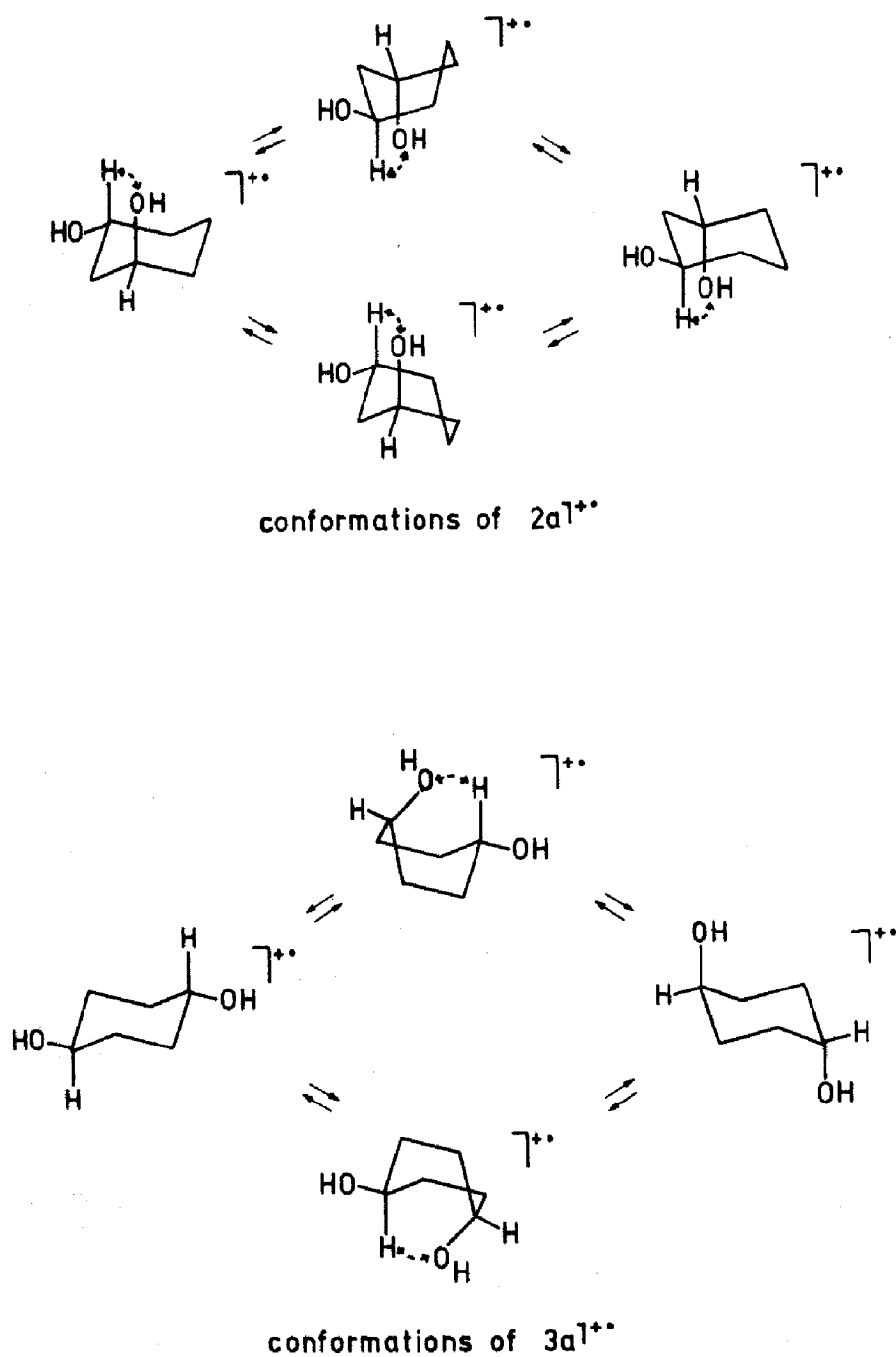
Scheme 3

obtained for labelled derivatives, although no definite answer can be given for this difference from the reactions of cyclohexanol [14] and decalin-1,4-diols [8].

A similar set of reaction mechanisms as for cyclohexanol, *cis*-cyclohexane-1,3-diol (2b) and *cis*-cyclohexane-1,4-diol (3b) also operates for the loss of H₂O from the molecular ions of the *trans*-diols 2a and 3a. This can be concluded from the curves of $k(t)$ versus τ for the loss of H₂O and D₂O, respectively, from 2a-1,3-*d*₂, 3a-1,4-*d*₂, 2a-*O-d*₂ and 3a-*O-d*₂ (Figs. 2 and 3), which are nearly identical with the FIK curves for the corresponding *cis* stereoisomers. However, for both compounds 2a and 3a, a process with a low activation energy for the loss of H₂O is possible, involving participation of an activated [15] CH group, which is not available in the fragmentation of the *cis* isomers. These are the transannular 1,3- and 1,4-eliminations, respectively, revealed by the loss of HDO from the molecular ions of 2a-1,3-*d*₂ and 3a-1,3-*d*₂. The increase of $k(t)_{\max}$ at τ_{\max} for 2a and 3a compared to 2b and 3b by a factor of 20 (Table 2) reflects the reduced activation energies of these processes. As in both compounds 2a and 3a the reduction of the dissociation energy of the C—H carbinol bond involved is the same (~ 20 kcal mol⁻¹), the effects on the activation energy and on $k(t)_{\max}$ for both transannular eliminations are expected to be very similar. However, the reactive conformations for the two eliminations are different, and also the conformational changes necessary for a transformation of the molecular ions from their most stable "ground-state" conformation to the reactive one. Hence the entropic requirements for the two transannular H₂O eliminations are different.

The activated 1,3-transannular elimination of H₂O from 2a ions requires a 1,3-diaxial interaction between a hydroxy group and an "activated" hydrogen atom. The corresponding orientation of the groups is already present in the ground-state chair conformation of 2a, with a distance of 2.5 Å between the oxygen atom of the hydroxy group and the hydrogen atom to be transferred* (Scheme 4). A similar (quasi-1,3-diaxial) orientation and distance between the reacting groups is found for the boat conformation of 2a. Furthermore, the two chair-conformations are identical with respect to the orientation of one axial hydroxy group and one "activated" hydrogen atom. As a consequence, most molecules of 2a are field-ionized directly into the

* The distances between the atoms and groups have been determined from Dreiding models of the cyclohexanediols. It is assumed that bond lengths and bond angles in the neutral molecule and the molecular ion are identical.



Scheme 4

reactive conformation for the activated 1,3-elimination of H_2O from the molecular ions. This explains the unique high value of $k(t)$ at short reaction times τ for $2a$ among the isomeric cyclohexanediols and the relatively small rise of $k(t)$ with increasing τ (by a factor of 2).

The conformations with the shortest distance (1.7 \AA) between one of the hydroxy groups and an "activated" hydrogen atom in $3a$ are the boat conformations. The reactive conformation for the activated 1,4-transannular

elimination of H₂O from 3a ions should correspond closely to this boat form. However, the boat conformation of 3a is ~ 7 kcal mol⁻¹ less stable than the ground-state chair conformation with both hydroxy groups in an equatorial position [17]. (The other chair conformation, with two axial hydroxy groups, is 1–2 kcal mol⁻¹ above the ground-state conformation [17]). The temperature of the molecules of 3a evaporating from a solid sample at 60°C into the ionization chamber at 270°C under high-vacuum conditions is ill-defined but even at 270°C, by far the majority of the molecules will be in one of the chair conformations. Hence in contrast to 2a, most molecules of 3a will not be in the reactive conformation for the 1,4-transannular elimination of H₂O, but have to change their conformation before reaction. In agreement with these considerations are the much lower values of $k(t)$ at small τ for 3a compared to 2a, and the steep increase of $k(t)$ with τ (by a factor of 10). This increase of $k(t)$ must be at least partly due to the excitation energy of molecular ions of 3a being used to change their conformation into the reactive one, and thus exhibiting a delayed fragmentation behaviour. The reactive conformation does not necessarily correspond to the boat form of 3a, but may also be a somewhat more stable twist-conformation with a distance of ~ 2.5 Å between the hydroxy group and the "activated" hydrogen atom to be transferred during the loss of H₂O.

A delayed loss of H₂O via a 1,4-transannular elimination has also been observed for the molecular ions of some decalin-1,4-diols having the appropriate orientation of the hydroxy groups [8]. With these compounds, the 1,4-elimination of H₂O reaches $k(t)_{\max}$ at $\tau_{\max} = 3 \times 10^{-9}$ s. For the 1,4-elimination from 3a ions τ_{\max} is much shorter (1.1×10^{-10} s) and close to the value observed for the loss of H₂O from cyclohexanol ions via a (not activated) 1,4-elimination [14]. This may reflect the greater conformational mobility of a cyclohexane ring compared to the decalin system, in which the chair–boat transformation of the hydroxylated cyclohexane ring is hampered by the attached second ring [8]. Maxima of the normalized rate constants at reaction times around 10^{-10} s have also been observed for other elimination reactions involving hydrogen-atom migrations in the molecular ions. Examples are the elimination of H₂O from hexanol ions [18], alkene elimination from the molecular ions of ethyl benzoate [19] and phenylhexanone [20] via a McLafferty rearrangement, and fragmentations of methyl isobutyrate [21]. A common feature of these processes is hydrogen-atom transfer by a cyclic transition state, and it is possible that the transfer precedes the fragmentation step, in a two-step mechanism. The maxima in the curves of $k(t)$ versus τ in the same range of τ -values for all these fragmentations may be linked to the preceding hydrogen-atom transfer step [21]. This would explain why maxima of $k(t)$ for the loss of H₂O from the molecular ions are observed at similar values of τ_{\max} (see Table 1) for all cyclohexanediols with the exception of 1a and 1b. Nevertheless, the unique behaviour of *trans*-cyclohexane-1,3-diol (2a) and *trans*-cyclohexane-1,4-diol (3a) with respect to the high values of $k(t)$ for H₂O elimination at small τ

and the steep increase in the rate constants for these processes clearly show that the conformations and conformational changes of the molecular ions are an important factor in the unimolecular reactions of these ions.

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