5 explains why hydroxide ion does not participate in the collapse of the intermediate above pH 11 as occurs with N-acetylpyrrole (see eq 4). Such a mechanism would produce an intermediate with a triple negative charge.

The proposed mechanism obeys the steady-state rate law given in eq 7.[34] When $K_1[OH^-] \gg 1$ (above pH

$$k_{obsd} = \frac{k_1 k_3 K_1 K_2 [OH^-]^2}{[k_2(1 + K_2[OH^-]) + } \qquad (7)$$
$$k_3 K_2[OH^-]][1 + K_1[OH^-]]$$

(34) $K_1 = [A^-]/[HA][OH^-]$; $K_2 = [A^{2-}]/[A^-][OH^-]$.

9.6 where greater than 90% of the substrate is anionic), the equation simplifies to eq 8. When $K_2[OH^-] \gg 1$

$$k_{obsd} = \frac{k_1 k_3 K_2 [OH^-]}{k_2(1 + K_2[OH^-]) + k_3 K_2[OH^-]} \qquad (8)$$

(above pH 11), the rate expression further simplifies to eq 9. Thus the observed rate constant becomes independent of the pH, in accord with experiment.

$$k_{obsd} = k_1 k_3/(k_2 + k_3) \qquad (9)$$

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Elimination of Water from Hexanol at 10^{-11} to 10^{-5} Second Following Field Ionization

P. J. Derrick,* A. M. Falick, and A. L. Burlingame[1]

Contribution from the Space Sciences Laboratory, University of California, Berkeley, California 94720. Received July 8, 1972

Abstract: The elimination of water from hexanol following field ionization (FI) has been studied at times from 10^{-11} to 10^{-5} sec. Investigation of the deuterated species hexanol-3,3-d₂ and hexanol-4,4-d₂ firmly establishes that the elimination of water involves hydrogen from C-3 as well as from C-4. Phenomenological rate constants $\bar{k}(t)$ have been calculated as functions of time from 10^{-11} to 10^{-5} sec for the process involving transfer of hydrogen from C-3 *via* a five-membered cyclic transition state and for that involving transfer from C-4 *via* a six-membered cyclic transition state. Comparison of the kinetics of the two processes suggests that the six-membered transition state is thermodynamically favored over the five membered; for the most energetic ions (produced by FI), however, the reactions *via* the two transition states occur with equal probability. It is opined that the frequency factors for the five- and six-membered transition states are both of the same order of magnitude (10^{10} sec⁻¹). Hydrogen-deuterium randomization is unimportant at times less than 10^{-9} sec following FI and probably at longer times as well. We suggest that the conclusions of the electron impact studies on hexanol have overestimated the importance of transfer of hydrogen from C-4 in the loss of water.

The elimination of water from alcohols to form what is formally an ionized olefin can be observed following both electron impact (EI) and field ionization (FI). EI measurements[2-5] on a variety of deuterium-labeled aliphatic alcohols indicate that the process is not a 1,2 elimination analogous to thermal dehydration.[6] Rather, the loss of water following EI involves the transfer of hydrogen to the hydroxyl group from more remote positions in the alkyl chain.[7] The EI studies suggest that with hexanol 90% of the hydrogen is transferred from C-4, while the remainder *appears* to come from C-3 (ref 5) (and possibly from C-5 as well[4]). It is not, however, possible to conclude from the EI data that hydrogen transfer occurs directly from C-3 to the hydroxyl *via* a five-membered transition state, for

there exists the very real possibility that deuterium incorporated at C-3 migrates to C-4 (*i.e.*, partial H/D randomization) prior to a specific 1,4 elimination. This difficulty in distinguishing between nonspecific hydrogen transfers (*i.e.*, transfer from more than one position in a chain to some active site) and specific hydrogen transfer preceded by partial H/D randomization is a fundamental limitation of the integrated view of events (over $\sim 10^{-6}$ sec) afforded by EI mass spectra.

We have studied the fragmentation of specifically deuterated hexanols using the unique capabilities of FI mass spectrometry,[8] and have established that the loss of water from hexanol is indeed nonspecific inasmuch as it involves hydrogen transfer from both C-3 and C-4 (and possibly from other sites to a small degree). Our prime objective in undertaking this FI study of hexanol was to measure and compare kinetics of two processes which are apparently similar, in that they eliminate the same neutral molecule, yet actually distinct, in that they involve cyclic transition states of different sizes. Differences in the kinetics of such processes can then be tentatively attributed to the differing cyclic transition

(1) John Simon Guggenheim Memorial Fellow, 1970-1972.

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(8) In sharp contrast to EI mass spectrometry, FI mass spectrometry provides a (time-) resolved view of events at times as short as the order of 10^{-12} sec; the kinetics of a reaction can be measured as a function of time over the interval 10^{-12}–10^{-5} sec.
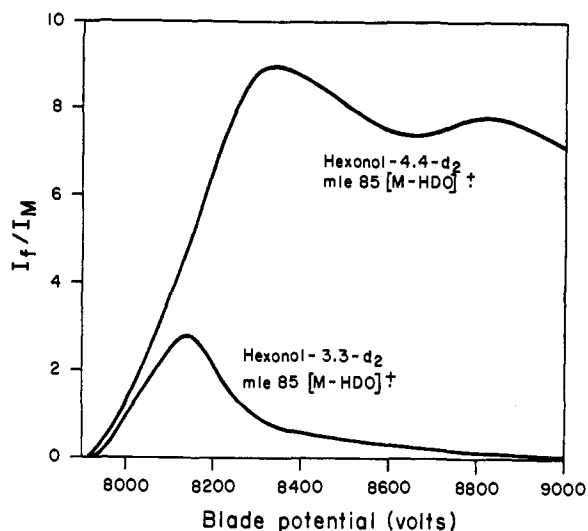
Figure 1. The experimental curves of ion currents I_f against blade potential for m/e 85 [M − HDO]$^+$ from hexanol-$3,3$-d_2 and hexanol-$4,4$-d_2. I_M is the ion current of the molecular ion M·$^+$ in the "normal" FI mass spectrum. The ion currents I_f at blade potential = 8000 V appear in the "normal" FI mass spectrum. Experimental data points have been omitted since their number is very high (120 points for each curve) and the scatter in the points is negligible.

Figure 2. Ion currents $I_f(t)$ due to m/e 84 [M − H$_2$O]·$^+$ and m/e 85 [(M + 1) − H$_2$O]·$^+$ from hexanol as a function of calculated parent ion lifetime. I_M is the ion current of the molecular ion M·$^+$ in the "normal" FI mass spectrum.

states, thereby providing some insight as to the properties of the transition states. It is of particular interest to investigate the influence of entropy as opposed to energy factors in deciding the preferred transition state size. That frequency factors (the entropy term in the quasi-equilibrium theory[9]) are important in determining the course of events induced by ionization has been emphasized only in recent years,[10] and our knowledge of the relationship between transition state size and the magnitude of the frequency factor is still exceedingly scant. The extent of the present understanding seems to be that loose transition states will tend to have higher frequency factors than rigid transition states.[11] The terms "loose" and "rigid" are, however, not very informative when considering cyclic transition states of complex molecules. The present paucity of information in mass spectrometry persists owing to the difficulty in estimating frequency factors by EI mass spectrometry. FI mass spectrometry is able to set lower limits for the magnitudes of frequency factors and thereby clarify the situation to a considerable extent.

We hope that the present study provides some further indication[12] of the exciting potential of FI mass spectrometry for kinetic and mechanistic investigations of the unimolecular gas-phase reactions induced by ionization. Such comparative kinetic studies as described above are possible only with FI mass spectrometry, since the wide time range (10^{-11}–10^{-5} sec) is inaccessible with EI techniques.[13]

Results

The "normal" FI mass spectrum of hexanol has been measured with a single-focusing instrument by Beckey.[14] FI of hexanol induces the formation of two fragment ions m/e 84 and 85 in the region between the blade and the cathode outside of the very high field (i.e., at times of 10^{-11}–10^{-8} sec). We have measured the kinetic energy distributions of these fragments from hexanol and of the fragments m/e 85 and 86 from hexanol-$3,3$-d_2 and hexanol-$4,4$-d_2 by the now well-established technique of varying the blade (ion accelerating) potential.[15–21] Varying the blade potential to make the measurements has only a very slight effect on the ionizing conditions.[22,23] The measured curves of ion current I_f against blade potential for m/e 85 from hexanol-$3,3$-d_2 and hexanol-$4,4$-d_2 are presented in Figure 1. The structure at around 8800 V in the hexanol-$4,4$-d_2 is due to fragment ions formed on the potential plateau between the focus electrodes. The phenomenon was discussed in an earlier paper.[12]

The kinetic energy distributions as represented by the curves of ion current I_f vs. blade potential are readily

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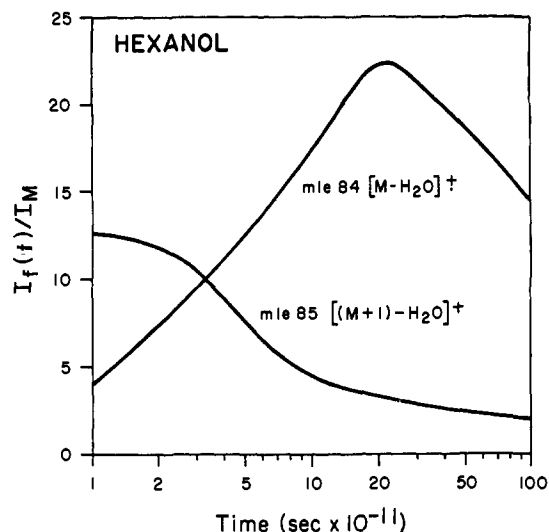
instrumentation have studied the kinetics of reactions induced by EI over times from 10^{-9} to 10^{-6} sec.

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(15) See H. D. Beckey, "Field Ionization Mass Spectrometry," Pergamon Press, New York, N. Y., 1971, pp 143–180, and references therein.

(16) P. J. Derrick and A. J. B. Robertson, presented at the 15th Field Emission Symposium, Bonn, Germany, Sept 1968.

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(23) P. J. Derrick, Ph.D. Thesis, University of London, 1969; P. J. Derrick and A. J. B. Robertson, Int. J. Mass Spectrom. Ion Phys., 10, 315 (1973).
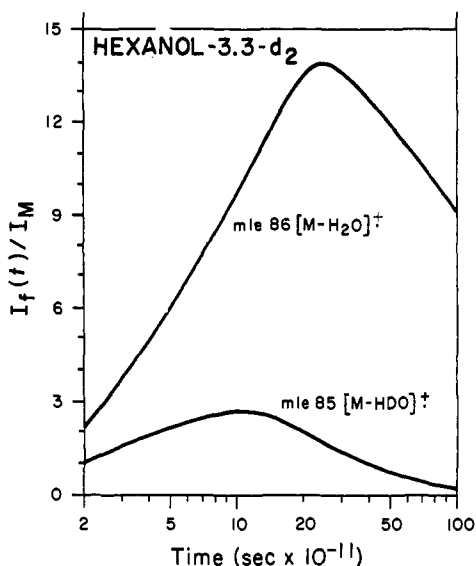
Figure 3. Ion currents $I_f(t)$ due to m/e 85 [M $-$ HDO]$\cdot^+$ and m/e 86 [M $-$ H$_2$O]$\cdot^+$ from hexanol-$3,3$-d_2 as a function of calculated molecular ion lifetime. I_M is the ion current of the molecular ion M$\cdot^+$ in the "normal" FI mass spectrum.

Figure 4. Ion currents $I_f(t)$ due to m/e 85 [M $-$ HDO]$\cdot^+$ and m/e 86 [M $-$ H$_2$O]$\cdot^+$ from hexanol-$4,4$-d_2 as a function of calculated molecular ion lifetime. I_M is the ion current of the molecular ion M$\cdot^+$ in the "normal" FI mass spectrum.

transformed to curves of ion current $I_f(t)$ vs. parent ion lifetime (see Figures 2–4). The theory and the method used for this transformation are described in our earlier paper[12] and more fully elsewhere.[15,19,21]

The significance of the ion current $I_f(t)$ in Figures 2–4 needs to be discussed.[24] The ion current $I_f(t)$ of a fragment ion at any particular time represents the number of fragment ions formed within some time interval Δt. The magnitude of this interval depends on the parent ion mass, the fragment ion mass, the parent ion lifetime, and the kinetic energy resolution of the mass spectrometer.[12,15,21] Division of $I_f(t)$ at a particular time by the appropriate value of Δt yields the rate of reaction at that time. It follows that for fragment ions of similar mass formed from the same parent ion or from different parent ions of similar mass (as in any of the Figures 2–4) the ratio of the ion currents $I_f(t)$ at any particular time is equal to the ratio of the rates of formation of the fragments at that time.

Transitions in the first field-free region between the source and the electric sector were measured both by defocusing the electric sector analyzer[25,26] and by raising the blade potential.[12,21] Results are presented in Table I.

Although the measurement of reaction rates by FIMS is now well established, it still seems necessary to

state explicitly that reactions observed at times longer than a few $\times$ 10^{-11} sec after FI are neither surface reactions nor by the very high field.[12,15,21,27] There has accumulated over the past few years a considerable body of evidence to suggest that reactions following FI at these times are essentially similar in nature to the reactions induced by low energy EI (ca. 12 eV).[12,15,27,28]

Discussion

The m/e 84 and 85 fragments following FI of hexanol are identified as [M $-$ H$_2$O]$\cdot^+$ and [(M $+$ 1) $-$ H$_2$O]$^+$, respectively. The formation of (M $+$ 1)$^+$ is attributed to surface reaction. The maximum ion current $I_f(t)$ for m/e 84 [M $-$ H$_2$O]$\cdot^+$ occurs at $\sim 2 \times 10^{-10}$ sec (Figure 1), in fair agreement with the results of Beckey.[15] At times greater than a few $\times$ 10^{-11} sec (i.e., in the gas phase and outside of the high-field region in the immediate vicinity of the blade), the rate of formation of m/e 84 [M $-$ H$_2$O]$\cdot^+$ considerably exceeds that of m/e 85 [(M $+$ 1) $-$ H$_2$O]$^+$ even though the intensity of M$\cdot^+$ is approximately half that of (M $+$ 1)$^+$. The odd electron molecular ions M$\cdot^+$ are thus more reactive than the even electron pseudomolecular ions (M $+$ 1)$^+$.

The rate of formation of m/e 85 [(M $+$ 1) $-$ H$_2$O]$^+$ does, however, exceed that of m/e 84 [M $-$ H$_2$O]$\cdot^+$ inside the very high field (i.e., at time $<$ a few $\times$ 10^{-11} sec). This suggests that the loss of water from (M $+$ 1)$^+$ is a simple bond dissociation involving no rearrangement, since the rates of such reactions are generally enhanced by the high field around the emitter.[29] Rearrangement reactions tend to be much less affected by the high field.[30] The simple dissociation is consistent with the additional hydrogen of (M $+$ 1)$^+$ being attached to the oxygen, such that rupture of the C–O

Table I. The Ratios of the Intensities of the Transitions 104 $\rightarrow$ 86 (M$^+$ $\rightarrow$ [M $-$ H$_2$O]$\cdot^+$) and 104 $\rightarrow$ 85 (M$^+$ $\rightarrow$ [M $-$ HDO]$\cdot^+$) in the First Field-Free Region (i.e., at $\sim 2 \times 10^{-6}$ sec) with Hexanol-$3,3$-d_2 and Hexanol-$4,4$-d_2

Hexanol-$3,3$-d_2	$I_{104 \rightarrow 86}/I_{104 \rightarrow 85}$	$>20^a$
Hexanol-$4,4$-d_2	$I_{104 \rightarrow 85}/I_{104 \rightarrow 86}$	5

^{a} The transition 104 $\rightarrow$ 85 could in fact not be detected with hexanol-$3,3$-d_2. The upper limit for the ratio is set by the signal to noise ratio for $I_{104 \rightarrow 86}$.

(24) For a fuller discussion, see ref 15, 19, and 21.
(25) M. Barber and R. M. Elliott, Proceedings of the 12th Annual Conference on Mass Spectrometry and Allied Topics, Montreal, 1964.
(26) J. H. Beynon, R. A. Saunders, and A. E. Williams, *Nature (London)*, 204, 67 (1964).

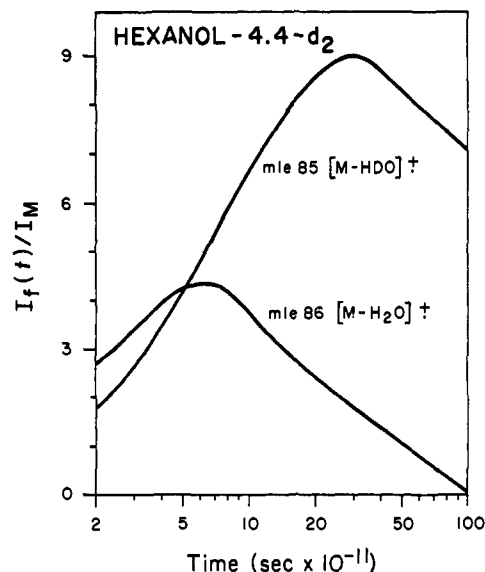(27) K. Levsen and H. D. Beckey, *Int. J. Mass Spectrom. Ion Phys.*, 7, 341 (1971).
(28) P. J. Derrick, A. M. Falick, and A. L. Burlingame, unpublished data.
(29) This is the phenomenon of "field dissociation"; see ref 15, p 127ff, for a full discussion.
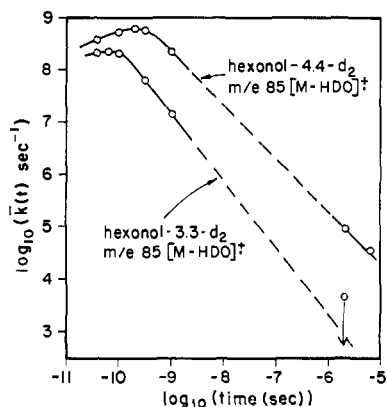(30) See ref 15, p 291ff, for a discussion.

Figure 5. The logarithm of the phenomenological rate constant $\bar{k}(t)$ for the formation of m/e 85 [M $-$ HDO]$^+$ from hexanol-$3,3$-d_2 and hexanol-$4,4$-d_2 calculated as a function of the logarithm of molecular ion lifetime. For each reaction, values of $\bar{k}(t)$ are calculated at five different times in the range 10^{-11}–10^{-9} sec and at one or two times at 10^{-6}–10^{-5} sec (see the points on the curves). The point at 10^{-6} sec for hexanol-$3,3$-d_2 represents the *maximum* possible rate constant. The point at $\sim 1 \times 10^{-5}$ sec for hexanol-$4,4$-d_2 is based on the metastable intensity in the "normal" FI mass spectrum, *i.e.*, the transition in the second field-free region. The curves have been corrected to allow for the increase in emission on raising the blade potential.[15]

bond effects the elimination of water. If this is the case, the loss of water from (M + 1)$^+$ probably does not involve any of the hydrogens attached to carbon atoms.

The m/e 85 and 86 fragments from hexanol-$3,3$-d_2 and hexanol-$4,4$-d_2 are identified as [M $-$ HDO]$\cdot^+$ and [M $-$ H$_2$O]$\cdot^+$, respectively. The loss of water from (M + 1)$^+$ produces an m/e 87 fragment. The deuterium incorporation in hexanol-$3,3$-d_2 and hexanol-$4,$-4-d_2 is better than 95 atom % (see Experimental Section). The results have not been corrected for isotopic impurity. The formation of m/e 85 (M $-$ HDO)$^+$ at times of 10^{-11}–10^{-9} sec firmly establishes hydrogens from both C-3 and C-4 are involved in the loss of water from hexanol. The possibility that partial H/D randomization precedes fragmentation at times of 10^{-11} to 10^{-9} sec can be dismissed.[31] Randomization will tend to favor the formation of m/e 86 over m/e 85 in both hexanol-$3,3$-d_2 and hexanol-$4,4$-d_2 (with complete randomization of all 12 H and 2 D, the ratio of m/e 86 to m/e 85 would be 73:27 in the absence of isotope effects), but no such trend is detectable in the ion current $I_t(t)$-time curves (Figures 3 and 4). Furthermore, if randomization began at such short times as 10^{-11} to 10^{-9} sec, it would be expected to be complete within 10^{-6} sec (ref 32) (*cf.* cyclohexene[12]). In fact, the transitions in the first field-free region at 10^{-6} sec (Table I) reveal very little, if any, H/D randomization. With hexanol-$3,3$-d_2 the only detectable decomposition of the molecular ion in the first field-free region is $104 \rightarrow 86$. This suggests that at these times (10^{-6} sec) hydrogen transfer from C-3 is insignificant (relative to

(31) It is conceivable that partial H/D randomization occurs in surface reactions. The experimental data [23,28] accumulated to date suggest, however, that this is not the case. Further, Beckey[15] has reported the loss of HDO following FI of hexanol-$3,3$-d_2 under conditions such that surface reactions responsible for (M + 1)$^+$, and hence probably all surface reactions, are suppressed.

(32) It is assumed that H/D randomization in hexanols is a low energy process. A high energy randomization process may be operative in certain alkane ions following EI;[28] however, the energy available from FI is probably too low for such a process to be significant in hexanols.

transfer from C-4) in the elimination of water from hexanol. The observation of the transition $104 \rightarrow 86$ in the first field-free region with hexanol-$4,4$-d_2 could be due either to partial H/D randomization prior to transfer from C-4 (see ref 33) or to hydrogen transfer from some site other than C-3 or C-4.

Phenomenological rate constants $\bar{k}(t)$ (ref 34) have been calculated for the formation of m/e 85 [M $-$ HDO]$^+$ from hexanol-$3,3$-d_2 and hexanol-$4,4$-d_2 (see Figure 5) using the relationship in eq 1 discussed by

$$\bar{k}(t) = I_t(t)/I_M(t)\Delta t \qquad (1)$$

Beckey[15] and our earlier paper.[12] $I_M(t)$, the ion current of M$^+$ remaining undecomposed at time t, has been estimated as follows. Rates of formation for m/e 85 and 86 from both hexanol-$3,3$-d_2 and hexanol-$4,4$-d_2 are readily calculated by division of $I_t(t)$ by Δt, as discussed earlier. Rates can be calculated not only at 10^{-11}–10^{-9} sec but also at 10^{-6} and 10^{-5} sec from the intensities of the metastable transitions in the first and second field-free regions.[35] Curves of log (rate) against log (time) over the range 10^{-11}–10^{-5} sec can then be drawn up for each of the fragments assuming linearity between 10^{-9} and 10^{-6} sec (where there are no experimental points). The results of Tenschert and Beckey[15,36] provide some justification for this assumption. Values of $I_M(t)$ at different times are then calculated by simple integrations of the log–log curves. The rate constants in Figure 5 refer to the transfer of a deuterium atom, but it is reasonable to assume that similar differences occur for the transfer of hydrogen. We have found that the relationship between the rates of formation of m/e 86 from hexanol-$3,3$-d_2 and hexanol-$4,4$-d_2 closely resembles that between the rates of formation of m/e 85 from the two molecules (except, of course, that the roles are reversed, so that m/e 86 from hexanol-$3,3$-d_2 represents transfer from C-4).

To discuss the kinetic results in relation to transition state size it is necessary to make some intelligent assumptions as to the mechanisms of the two processes (see eq 2 and 3).[37] The first step in each process is in all
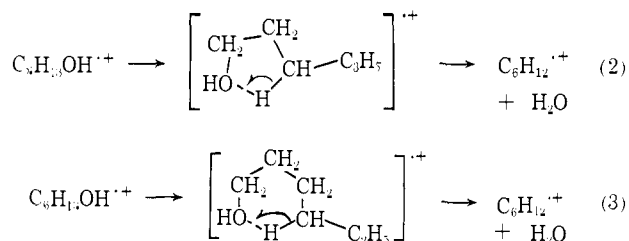
(33) It is quite conceivable in studying the elimination of water at times of 10^{-6} sec for partial randomization to be manifested in hexanol-$4,4$-d_2 but pass undetected in hexanol-$3,3$-d_2. With hexanol-$4,4$-d_2 (assuming transfer to be specific from C-4 at times of 10^{-6} sec), all possible H/D randomization reactions introduce H at the critical C-4 position, and the randomization is revealed by the loss of H$_2$O, whereas with hexanol-$3,3$-d_2, of all the conceivable H/D exchanges only that between C-3 and C-4 can be detected (as the elimination of HDO) when studying the loss of water. Moreover, the isotope effects will enhance the manifestation of randomization in hexanol-$4,4$-d_2 and suppress its manifestation in hexanol-$3,3$-d_2 [since isotope effects favor the loss of H$_2$O over the loss of HDO (see the final paragraph of the paper)].

(34) In an earlier paper,[12] we referred to the phenomenological rate constant $\bar{k}(t)$ as an "average rate constant" (after Beckey[15]). We now prefer the name "phenomenological rate constant" since this emphasizes that $\bar{k}(t)$ is an experimental quantity (even though our estimations of its values involve calculation), in contrast to the microscopic rate constant k which is a theoretical quantity (relating to an ideal situation in which all reactant ions possess the same amount of internal excitation energy). Moreover, the names "phenomenological" and "microscopic" emphasize that the relationship between these rate constants is closely analogous to that between the phenomenological and microscopic cross sections of ion–molecule reactions.

(35) No allowance has been made for the possible effects of partial H/D randomization at 10^{-6} sec. In the case of m/e 85 from hexanol-$3,3$-d_2 for which no metastable could be detected at 10^{-6} sec, the rate of formation is arbitrarily assumed to be 0.01 that of m/e 86 from hexanol-$3,3$-d_2.

(36) G. Tenschert and H. D. Beckey, *Int. J. Mass Spectrom. Ion Phys.*, 7, 97 (1971).

(37) We do not claim that the reactions necessarily occur in a stepwise fashion. It is possible that the transfer of hydrogen and the elimination of water are concerted events.

$$C_5H_{13}OH^{\cdot+} \longrightarrow \left[\begin{array}{c} CH_2\!-\!CH_2 \\ CH_2 \quad CH\!-\!C_3H_7 \\ HO\cdot\;\;H \end{array} \right]^{\cdot+} \longrightarrow \begin{array}{c} C_6H_{12}^{\cdot+} \\ +\ H_2O \end{array} \quad (2)$$

$$C_6H_{13}OH^{\cdot+} \longrightarrow \left[\begin{array}{c} CH_2 \\ CH_2 \quad CH_2 \\ HO\cdot\;H\;\;CH\!-\!C_2H_5 \end{array} \right]^{\cdot+} \longrightarrow \begin{array}{c} C_6H_{12}^{\cdot+} \\ +\ H_2O \end{array} \quad (3)$$

probability hydrogen transfer from C-3 or C-4 to the hydroxyl group via five- or six-membered cyclic transition states. It is the competition between these steps which will determine the relative success of the two processes (provided the transfer is not reversed to any significant extent). It is now assumed that long-lived intermediates play no significant role in the processes. That is to say, the elimination of H_2O subsequent to transfer is rapid in comparison to the hydrogen migration (or perhaps the elimination is concurrent with the migration). This is a reasonable assumption. The overall process $C_6H_{13}OH^{\cdot+} \rightarrow C_6H_{12}^{\cdot+} + H_2O$ is probably slightly exothermic or thermochemically neutral depending on the structure of the $C_6H_{12}^{\cdot+}$ fragment (from consideration of heats of formation).[38] A rearrangement $C_6H_{13}OH^{\cdot+} \rightarrow C_6H_{12}OH_2^{\cdot+}$ is probably endothermic. Thus the energy barrier to the elimination of H_2O from $C_6H_{12}OH_2^{\cdot+}$ is probably low. On the basis of the foregoing assumption, the kinetics of the formation of m/e 85 from hexanol-3,3-d_2 and hexanol-4,4-d_2 can be considered to reflect the kinetic characteristics of the two deuterium migrations.

It is reasonable to assume that the most energetic molecular ions decompose at the shortest times and the less energetic ions at the longer times. Furthermore, it should be borne in mind that the initial distribution of internal excitation energy is the same for both processes. Thus the variation in the phenomenological rate constants with time (Figure 5) indicates that in the most energetic molecules (formed by FI) the two processes via six- and five-membered transition states compete on approximately equal terms. As the energy of the molecules declines, however, so the process via a six-membered transition state is increasingly preferred over that via a five-membered transition state. The situation could alternatively be described by saying that the six-membered transition state is thermodynamically favored,[39] but that kinetically the two transition states are equally attractive (within the range of energies available through FI).

The positions of the maxima in the phenomenological rate constants $\bar{k}(t)$ (Figure 5) are significant and support the above conclusions. The maximum for m/e 85 from hexanol-3,3-d_2 ($\sim 1 \times 10^{-10}$ sec) occurs at a shorter time than that for m/e 85 from hexanol-4,4-d_2 ($\sim 3 \times 10^{-10}$ sec) (ref 40). Levsen and Beckey[27] sug-

(38) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, U. S. Government Printing Office, Washington, D. C., 1969.
(39) M. M. Green, R. J. Cook, J. M. Schwab, and R. B. Roy, *J. Amer. Chem. Soc.*, **92**, 3076 (1970), conclude that 1,4 elimination of water from cyclohexanol is a less energetic process than 1,3 elimination.
(40) These maxima reflect the fact that m/e 85 from hexanol-3,3-d_2 is formed at shorter times than m/e 85 from hexanol-4,4-d_2. Thus, 40% of the total m/e 85 from hexanol-3,3-d_2 is formed within 1×10^{-10} sec of ionization and 80% within 1×10^{-9} sec. The corresponding figures for m/e 85 from hexanol-4,4-d_2 are 5 and 35%, respectively. These estimates are based on the integrations of the log (rate) *vs*. log (time) curves performed in drawing up Figure 5.
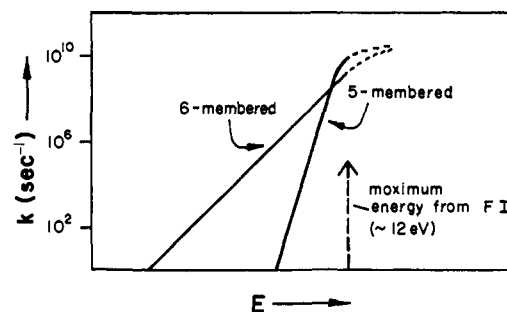

Figure 6. Schematic curves of microscopic rate constants k against internal excitation energy E for the formation of m/e 85 [M − HDO]$^+$ from hexanol-3,3-d_2 via a five-membered transition state and from hexanol-4,4-d_2 via a six-membered transition state.

gest that maxima in $\bar{k}(t)$ are a logical consequence of the necessity to invoke a distribution of microscopic rate constants k for adequate description of a reaction (the phenomenological rate constants $\bar{k}(t)$ represent some average of the microscopic rate constants k, as discussed in our earlier paper[12]). Making reasonable assumptions as to the form of the distribution of microscopic rate constants k, simple kinetic theory shows that the phenomenological rate constant $\bar{k}(t)$ will be at a maximum and constant value at times $< 1/k_{max}$ (ref 27) (k_{max} is the maximum k within the distribution). The curves in Figure 5 actually decline between the times of their maxima and 1×10^{-11} sec. We will, however, assume that the times of the maxima do approximately represent $1/k_{max}$, in which case k_{max} for the formation of m/e 85 from hexanol-3,3-d_2 is $\sim 1 \times 10^{10}$ sec^{-1} and that for the formation of m/e 85 from hexanol-4,4-d_2 is $\sim 3 \times 10^9$ sec^{-1}. This being so, at the *very highest energies available by FI the five-membered transition state is actually preferred over the six-membered*.

The conclusions reached so far allow schematic curves of microscopic rate constants k vs. internal energy E to be drawn up (Figure 6). The six-membered transition state is energetically more stable than the five-membered, and has the lower activation energy. The five-membered transition state yields the higher microscopic rate constant k at the maximum energy available from FI. Hence the curves cross. The forms of the curves (Figure 6) are perhaps rather unexpected. The prevalence throughout mass spectrometry of six-membered transition states in hydrogen transfers might have led one to predict that the process via the six-membered transition state would have had the higher rate constant k over the whole range of energies E. It appears that this is not the case. The steeper slope of the curve for the five-membered transition state can be attributed to a smaller number of active degrees of freedom s (referring to the quasi-equilibrium relationship $k = \sigma v[(E - E_0)/E]^{s-1}$) compared with the six-membered transition state.

The forms of the curves of k vs. E at energies higher than those available by FI cannot be deduced from the present measurements, so that the actual values of the frequency factors for the processes cannot be determined. It is, however, possible to set lower limits for the frequency factors from our results. The maximum microscopic rate constants determine that the frequency factor for the five-membered transition state is $\geq 5 \times 10^9$ sec^{-1} and that for the six-membered transi-

tion state is $\geq 2 \times 10^9$ sec^{-1}. (The symmetry factor σ is 2 for these reactions.) The importance of such estimations is that they do provide a sound basis for a more reliable knowledge of frequency factors. Yeo and Williams[41] have previously estimated frequency factors for unimolecular gas-phase rearrangements induced by EI. They calculated frequency factors of 3×10^{10} sec^{-1} for the six-membered cyclic transition state in the loss of methanol from methyl o-toluate and 3×10^6 sec^{-1} for the four-membered cyclic transition state in the loss of ethane from diethyl ketone. Any impression that the frequency factors of six-membered transition states tend to be greater than those of four-membered by factors of the order of 10^4 may, however, be seriously misleading, for the FI results reported here suggest that the dependence of frequency factors on the sizes of transition states may be much less dramatic. The frequency factor for the six-membered transition state in the loss of water from hexanol is probably of the order of 10^{10} sec^{-1} (it is $\geq 2 \times 10^9$ sec^{-1}, but probably does not exceed 1×10^{11} sec^{-1}) (ref 42). The frequency factor for the five-membered transition state is also very probably of the order of 10^{10} sec^{-1}.[43] The conclusion can be drawn that, although fundamental considerations demand that tighter transition states have lower frequency factors, the difference in the degree of "tightness," and hence in the magnitude of the frequency factors, between five- and six-membered transition states of similar natures within the same molecule may in some cases be very slight.

It is of interest to consider the implications of the FI results to the EI studies of hexanol. Meyerson and Leitch[5] concluded that, for $C_6H_{12}\cdot^+$ ions appearing in the normal mass spectrum of hexanol following 70-eV EI, 91% of the extra hydrogen lost as water came from C-4 and 9% probably from C-3 (none from C-5 or C-6). Benz and Biemann[4] reached rather similar conclusions. Yet it must be realized that the $C_6H_{12}\cdot^+$ ions which are sufficiently long-lived to appear in the normal EI mass spectrum represent only about 5% of the total number of $C_6H_{12}\cdot^+$ ions formed from the molecular ion.[5] The remaining 95% are short-lived and decompose to secondary fragments ($C_4H_7^+$, $C_4H_8\cdot^+$, $C_5H_9^+$) prior to detection. The figures of 91% hydrogen from C-4 and 9% probably from C-3 will therefore only give reliable indication of the overall importance of transfer from C-3 and C-4 if the 5% of $C_6H_{12}\cdot^+$ appearing in the EI mass spectrum is a representative cross section of the whole number of $C_6H_{12}\cdot^+$ ions (i.e., including those that decompose prior to detection). This is, however, unlikely to be the case. The 5% of $C_6H_{12}\cdot^+$ ions appearing in the EI mass spectrum are evidently the longest lived fraction of the whole number of $C_6H_{12}\cdot^+$ ions, so that it is reasonable to conclude that they are also a very low energy fraction (compared to a higher energy fraction which decompose). It can be assumed that low energy $C_6H_{12}\cdot^+$ fragments will be formed from low energy molecular ions. Study of the $C_6H_{12}\cdot^+$ appearing in the EI mass spectrum, therefore, does not give an indication of the overall relative importance of transfer from C-3 and C-4, but rather an indication of the relative importance of transfer from the two sites in a 5% sample of very low energy reactant molecular ions. Thus the implications of our FI results to the EI studies become apparent. The FI results revealed that in the low energy molecular ions transfer from C-4 predominates over transfer from C-3, but that in higher energy ions the two processes are of comparable importance. The EI studies detect the loss of water only from the 5% low energy molecular ions (as established above), so that predominant transfer from C-4 should be observed. This is the case (the 91% from C-4). In the higher energy molecular ions following EI, however, transfer from C-3 is expected to be comparable in importance to transfer from C-4. The products of these reactions, however, decompose and pass undetected. The conclusion is reached, therefore, that if *all* the reactant molecular ions following 70-eV EI could be taken into account, transfer from C-4 to eliminate water would be found to be considerably *less* important than the generally accepted figure of 90%.[44] Transfers from C-3 would be considerably more important than the generally accepted figure of a few per cent. This conclusion is given some support by the degree of label retention in the secondary fragments following 70-eV EI of deuterated hexanols.[5] For example, with hexanol-4,4-d_2, under 70-eV EI conditions 28% of the $C_5H_9^+$ species formed by loss of $CH_3\cdot$ from $C_6H_{12}\cdot^+$ species have retained *both* of the deuterium labels (to retain both deuteriums the initial loss of water must involve transfer from some site other than C-4).

It remains only to point out that an isotope effect is operative in the loss of water from the deuterated hexanols following FI. It is evident from Figures 3 and 4 that the formation of m/e 86 from hexanol-3,3-d_2 occurs to a significantly greater extent than the formation of m/e 85 from hexanol-4,4-d_2 (note the difference in scale on the y axis between the figures). Further, the maximum in the m/e 86 curve (Figure 3) occurs at a shorter time than that in the m/e 85 curve (Figure 4). Similar differences are observed between the m/e 86 curve with hexanol-4,4-d_2 and the m/e 85 curve with hexanol-3,3-d_2. The differences cannot be satisfactorily explained by assuming transfer from some position other than C-3 or C-4, although this may be a contributing factor. To account for the differences in intensities between m/e 86 in hexanol-3,3-d_2 and m/e 85 in hexanol-4,4-d_2, such transfer would have to occur to an extent almost comparable to that from C-4. If this were the case, then the intensities of m/e 86 from hexanol-4,4-d_2 would be considerably higher than the values actually observed. It is, therefore, concluded that the differences are due to isotope effects. The rates of the reactions over the interval 10^{-11} to 10^{-9} sec are diminished on replacing H with D by an approxi-

(41) A. N. H. Yeo and D. H. Williams, *Chem. Commun.*, 956 (1969).

(42) Based on an estimation of time required by the molecule to achieve the steric configuration necessary for the formation of the ring; see ref 27 for a discussion.

(43) Further in our FI study of cyclohexene,[12] is was found that 1,3 allylic rearrangements occur within times of the order of 10^{-11} sec. The frequency factor of the four-membered transition state for this rearrangement must, therefore, be of the order of 10^{10} sec^{-1}. Thus we have a four-, a five-, and a six-membered transition state all with frequency factors of the order of 10^{10} sec^{-1}.

(44) Transfer from C-4 is, however, this important following FI. Over the time interval of 2×10^{-6} sec following FI, hexanol-3,3-d_2 yields 94% of m/e 86 and only 6% of m/e 85. Hexanol-4,4-d_2 yields 92% of m/e 85 and 8% of m/e 86. The figures are based on the integrations of log (rate) *vs.* log (time) curves performed in drawing up Figure 5. The high figures of ~90% for transfer from C-4 are readily explicable in terms of discrimination in favor of the low energy reaction following a low energy ionization process.

mately constant factor of ≤ 1.6 (the factor is ~ 1.6 assuming transfer occurs solely from C-3 and C-4). The isotope effect could arise in the transfer of H (D) from the alkyl chain to the oxygen.

Experimental Section

The FI mass spectrometer is a modified Du Pont (C.E.C.) 21-110B double-focusing instrument.[21] The standard Du Pont combination FI/EI ion source is used with the electron collimating magnet removed to avoid mass discrimination. Source temperatures of between 50 and 150° were employed for the measurements described. Uncoated stainless steel razor blades kindly supplied by Schick were employed as emitters. The fragment ion currents I_t are measured as a function of blade potential on an x–y recorder. The blade potential is varied incrementally in 10-V steps. The

maximum fragment ion currents are of the order of 10^{-12} A at the beam monitor.

The deuterated hexanols were kindly supplied by Dr. W. H. McFadden. The preparation and estimation of purity of these molecules have been described.[45] To confirm results, the experiments were repeated with molecules synthesized in our laboratory.[46]

(45) W. H. McFadden, L. E. Boggs, and R. G. Buttery, *J. Phys. Chem.*, 70, 3516 (1966).
(46) The hexanols were intermediates in syntheses of deuterated hexanols: P. J. Derrick, A. M. Falick, S. Lewis, and A. L. Burlingame, to be submitted for publication.

A Reexamination of Electronic Effects in Ring-Substituted Phenyl Esters. Correlation of Spectral and Kinetic Properties with σ^0

Louis A. Cohen*[1] and Sho Takahashi

Contribution from the Laboratory of Chemistry, National Institute of Arthritis and Metabolic Diseases, National Institutes of Health, Bethesda, Maryland 20014. Received June 19, 1972

Abstract: The ultraviolet K bands for para-substituted phenyl acetates differ in wavelength from those of the corresponding monosubstituted benzenes by 8–10 nm, regardless of the electronic nature of the para substituent. Similarly, a constant displacement is observed in the K bands for 6-substituted hydrocoumarins. On the basis of these results, phenyl esters and lactones are considered to be devoid of "through resonance" between the aryl–oxygen atom and the para substituent. Although the ester plane of a phenyl ester is considered to be perpendicular to the benzene plane, steric inhibition is only an apparent cause for reasonance uncoupling; the true cause is the thermodynamic preference by the oxygen atom to overlap with the ester carbonyl rather than with the benzene ring. In support of this argument, the infrared carbonyl-stretching frequencies for 48 mono- and polysubstituted phenyl hydrocinnamates are shown to correlate ($r = 0.9997$) with σ^0 (or $\Sigma\sigma^0$) for the ring substituents, including a number of ortho substituents. Values of σ_o^0 (for nonpolar media) are derived by calculation: $\sigma_o^0(R) = \sigma_p^0(R) + 0.39\sigma^*$-$(RCH_2)$. Values of σ^0 for hydroxylic media have been reevaluated on the basis of 24 sets of data for systems in which resonance coupling of the reaction site with the benzene ring is improbable. These σ^0 values are, in turn, used to correlate 33 sets of data on the intermolecular reactions of phenyl esters with various nucleophiles. The excellent correlations obtained serve to demonstrate that σ^0 is the appropriate parameter to be used in such correlations. Intramolecular reactions of phenyl esters, on the other hand, show a better correlation with σ^-. It is tentatively considered that formation of a tetrahedral intermediate is rate limiting in intermolecular reactions of phenyl esters with nucleophiles, but that breakdown of a tetrahedral intermediate is rate limiting in intramolecular cases.

The properties of aromatic systems, in which a functional group is separated from the ring by one or more methylene carbons, have been used to derive values of σ^0, a substituent parameter considered free of any component due to significant π-electronic interaction with the side-chain functional group.[2] Obviously, such systems are also devoid of "through resonance," the coupling of ring substituents with the functional group *via* the aromatic π cloud. It has not been generally recognized, however, that phenolic esters fall into the same category, *i.e.*, that acylation of a phenol serves to uncouple virtually all resonance overlap between the phenolic oxygen atom and the aromatic π system. In this paper we present several spectroscopic

studies in support of the generalization and examine its consequences in kinetic and mechanistic studies.

Space-filling models show quite clearly that phenyl acetate is not a planar molecule. Whether the s-cis (**1a**) or s-trans (**1b**) conformation is assigned to the ester
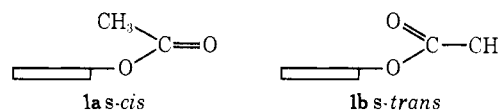
group, ortho substituents as small as hydrogen seem to be sufficient to prevent the achievement of coplanarity with the benzene ring. Dipole moment studies[3] are

(1) Author to whom correspondence should be addressed.
(2) R. W. Taft, Jr., *J. Phys. Chem.*, 64, 1805 (1960).

(3) (a) M. Aroney, R. J. W. Le Fèvre, and S.-S. Chang, *J. Chem. Soc.*, 3173 (1960); (b) O. Exner, Z. Fidlerová, and V. Jehlička, *Collect. Czech. Chem. Commun.*, 33, 2019 (1968); (c) V. Balish and K. Gana-