Mechanistic and Kinetic Studies at 10^{-11}–10^{-5} Sec of the Unimolecular Gas-Phase Reactions Induced by Field Ionization of Cyclohexene and Cyclohexene-*3,3,6,6-*d_4

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Abstract: The major unimolecular gas-phase reactions induced by field ionization (FI) of cyclohexene and cyclohexene-*3,3,6,6-*d_4 have been studied at times from 10^{-11} to 10^{-5} sec. Randomization or "scrambling" of the hydrogens and deuteriums in cyclohexene-*3,3,6,6-*d_4 is observed to begin within 1×10^{-11} sec and to be complete within 1×10^{-9} sec. It is proposed that randomization is the result of successive 1,3-allylic rearrangements. Mechanisms are proposed for the formation of $(M - C_2H_4)\cdot^+$, $(M - CH_3)^+$, and $(M - C_3H_5)^+$ from cyclohexene following FI. The electron impact (EI) mass spectra of cyclohexene and cyclohexene-*3,3,6,6-*d_4 have been measured at high and low ionizing energies, and are discussed in relation to the FI results. The reactions induced by low-energy EI (~12 eV) appear to be essentially similar in nature to the reactions occurring at 10^{-11}–10^{-5} sec following FI.

Field ionization mass spectrometry (FIMS) permits the observation and measurement of rates of the competing and consecutive unimolecular gas-phase reactions induced by ionization of a molecule over a time range from 10^{-12} to 10^{-5} sec.[2–7] Time intervals (in the reactant ion lifetime) as short as 10^{-12} sec are resolved. The rate measurements represent a wealth of novel kinetic data on simple chemical reactions, since comparable measurements at such short times cannot be made with any other technique presently available to the chemist. Furthermore, the highly resolved view of events (in terms of time) allows the various competing and consecutive reactions (including the reactions responsible for the phenomenon of isotopic randomization or "scrambling") to be clearly identified.

Attempts to understand unimolecular gas-phase reactions induced by ionization have previously been hampered by reliance on electron impact (EI) and other mass spectrometric techniques which present an *integrated* view of all reactions occurring within the long and arbitrary time interval of 10^{-6} sec. Such techniques can fail to distinguish among competing or consecutive reactions and provide little kinetic data on reactions occurring within 10^{-6} sec.[8] In one sense, FIMS by affording the highly *resolved* view adds a new dimension to mass spectrometry.

The unique capabilities of FIMS have, however, been little exploited. The extensive studies of Beckey and his colleagues[2] have tended to emphasize the physical aspects of FI measurements, in particular the relationship between experimentally determined rate constants and the quasiequilibrium theory. We have, therefore, initiated[9] a program in our laboratory with a view to establishing FIMS as a powerful and possibly essential technique for mechanistic and kinetic studies of unimolecular gas-phase reactions induced by ionization.

Cyclohexene was chosen for study since its reactions following ionization were previously not well understood. Furthermore, the cyclohexene molecule holds more than intrinsic interest because of the common occurrence of cyclohexenoid structures in natural products, such as terpenes. The FI study affords a much deeper and surer understanding of the reactions of the cyclohexene ion than that possible on the basis of EI measurements alone, and, we feel, demonstrates convincingly the tremendous potential of FIMS for mechanistic and kinetic studies of such reactions.

Experimental Section

FI measurements were made with a modified DuPont (C.E.C.) 21-110B double-focusing mass spectrometer.[6,10] The standard DuPont combination FI/EI ion source was employed with the electron collimating magnet removed to avoid mass discrimination. The source temperature was maintained at 100° during all experiments.

The EI mass spectra were measured on a DuPont (C.E.C.) 21-492 mass spectrometer connected to the XDS Sigma 2 computer data acquisition system.[11]

The cyclohexene-*3,3,6,6-*d_4 supplied by Merck Sharp and Dohme was estimated to have an isotopic purity of greater than 99 atom %. The identity of the deuterated molecule was confirmed by nmr.

Results

The "normal" FI mass spectra of cylohexene and cyclohexene-*3,3,6,6-*d_4 are reproduced in Figure 1. The spectra were measured with the potential applied to the blade (8000 V) approximately equal to the accelerating potential (V_N) necessary for ions to be trans-

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[1] John Simon Guggenheim Memorial Fellow, 1970–1972.

[2] (a) H. D. Beckey, H. Hey, K. Levsen, and G. Tenschert, *Int. J. Mass Spectrom. Ion Phys.*, 2, 101 (1969); (b) H. D. Beckey, "Field Ionization Mass Spectrometry," Pergamon, Elmsford, N. Y., 1971, pp 143–180.

[3] P. J. Derrick and A. J. B. Robertson, presented at the 15th Field Emission Symposium, Bonn, Germany, Sept 1968.

[4] P. J. Derrick and A. J. B. Robertson, *Proc. Roy. Soc., Ser. A*, 324, 491 (1971).

[5] P. Schulze, W. J. Richter, and A. L. Burlingame, *Proc. 17th Annu. Conf. Mass Spectrom. Allied Top., 1969*, 454 (1970).

[6] A. L. Burlingame, A. M. Falick, G. W. Wood, P. Schulze, and W. J. Richter, *Proc. 18th Annu. Conf. Mass Spectrom. Allied Top., 1970*, B416 (1971).

[7] P. Schulze and W. J. Richter, *Int. J. Mass Spectrom. Ion Phys.*, 6, 131 (1971).

[8] By means of special electron impact mass spectrometric techniques, Ottinger and his colleagues have been able to measure the rates of reactions at 10^{-9}–10^{-6} sec [*Z. Naturforsch. A*, 22, 20 (1967)].

[9] See P. J. Derrick, A. M. Falick, J.-P. Pfeifer, and A. L. Burlingame, submitted to *J. Amer. Chem. Soc.* for publication.

[10] A. M. Falick, P. J. Derrick, J.-P. Pfeifer, and A. L. Burlingame, manuscript in preparation.

[11] D. H. Smith, R. W. Olsen, F. C. Walls, and A. L. Burlingame, *Anal. Chem.*, 43, 1796 (1971).

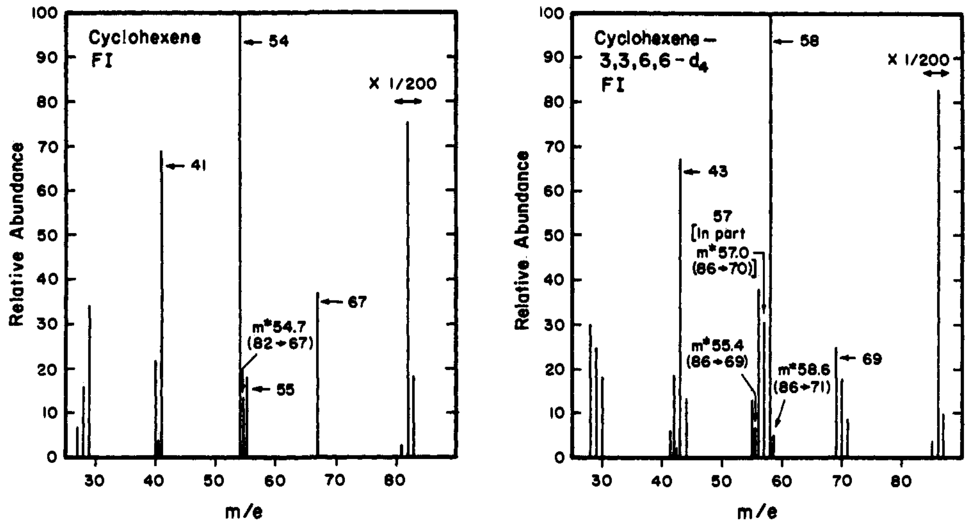

Figure 1. The "normal" FI mass spectra of cyclohexene and cyclohexene-*3,3,6,6-d$_4$*; blade potential = 8000 V.

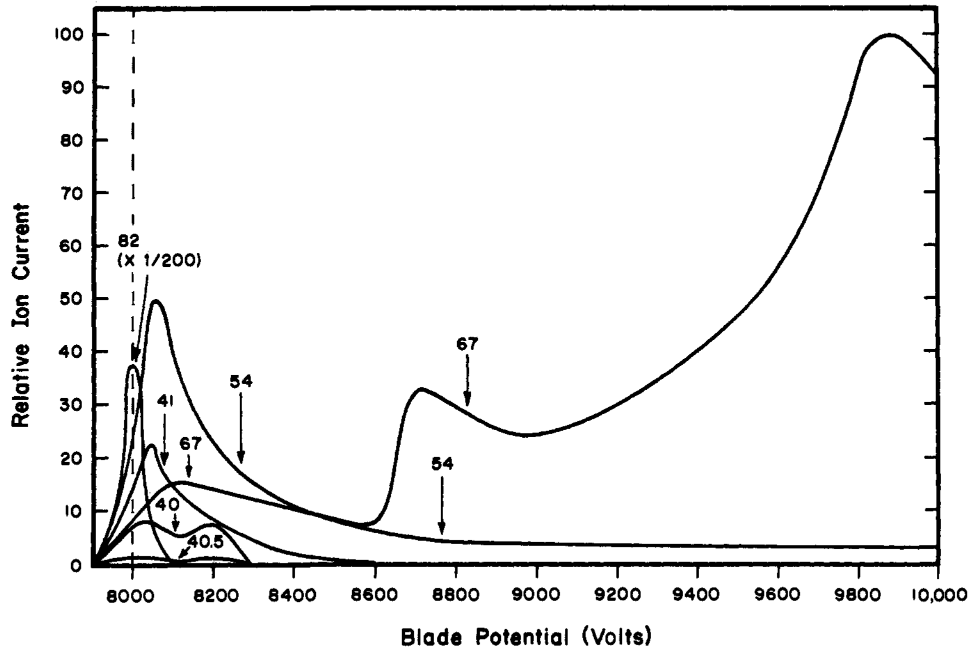

Figure 2. Ion currents as a function of blade potential for the molecular ion and the important fragment ions following FI of cyclohexene. The ion currents at V_B = 8000 V constitute the "normal" FI mass spectrum.

mitted through the electric sector analyzer. Thus, the spectra display the ions formed in the immediate vicinity of the blade.

Profiles of ion current against blade potential (V_B) for the molecular ion and the important fragment ions following FI of cyclohexene are shown in Figure 2. The profiles are recorded on an XY plotter by focusing the magnetic analyzer on a particular ion and sweeping the blade potential. It is the ion currents at V_B = 8000 V which constitute the "normal" FI mass spectrum (Figure 1). The theory behind the measurement of such profiles has been discussed elsewhere,[2–4,10] so only a brief description need be given here.

The potential distribution within the FI source under "normal" operating conditions (*i.e.*, V_B = 8000 V) is shown schematically in Figure 3. The potential drops off very sharply on moving away from the blade and is very close to zero at the cathode slit. Fragment ions formed by decomposition between the blade and the cathode thus gain less kinetic energy than similar ions formed at the blade, and under "normal" operating conditions (V_B = 8000 V) do not pass through the electric sector analyzer. These ions can, however, be detected by raising the blade potential. Varying the blade potential does change the ionizing conditions, but these changes are very slight indeed due to the emission characteristics of a blade emitter.[12,13] The changes do not affect the results of the paper.

If a molecular ion M^+ formed at the blade decomposes at a potential V_1 to yield a fragment ion m^+, then m^+ passes through the electric sector when the relationship 1 is satisfied. eV_N is the translational energy

$$eV_N = eV_1 + em/M(V_B - V_1) \qquad (1)$$

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(12) See ref 2b, pp 58–68.

(13) P. J. Derrick, Ph.D. Thesis, University of London, 1969.

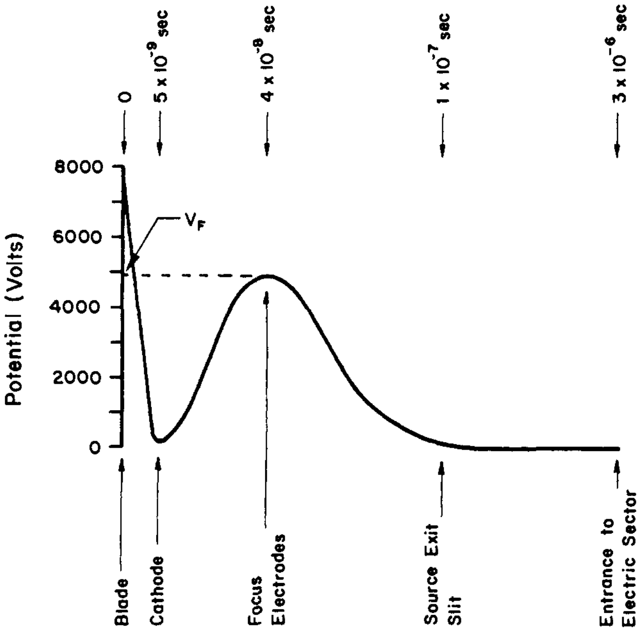

Figure 3. Potential distribution within the FI source for V_B = 8000 V. V_F is the potential between the focusing electrodes. The times of flight were calculated for an ion of *m/e* 82 formed at the blade.

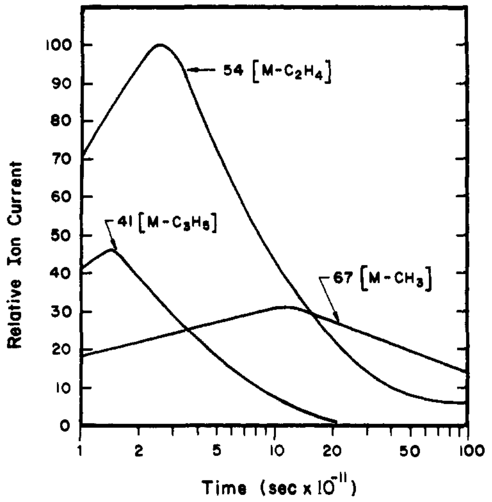

Figure 4. Ion currents $I_f(t)$ due to the major fragment ions formed following FI of cyclohexene as a function of the molecular ion lifetime.

required by an ion in order to traverse the electric sector. The value of V_B at which a fragment ion is detected defines through the relationship 1 the potential V_1 at which decomposition occurred. Given the potential distribution within the source, the time of flight of the ion M^+ to the potential V_1 can be calculated and can be considered as the lifetime of M^+ prior to decomposition. The profiles of ion current against blade potential (Figure 2) are thus transformed to curves of ion current $I_f(t)$ against lifetime of the molecular ion (Figure 4). (The lifetime of the molecular ion is *not* the ion *half-life.*) The methods employed for the calculation of the potential distribution within the FI source and for the calculation of the ion trajectories have been described.[14,15]

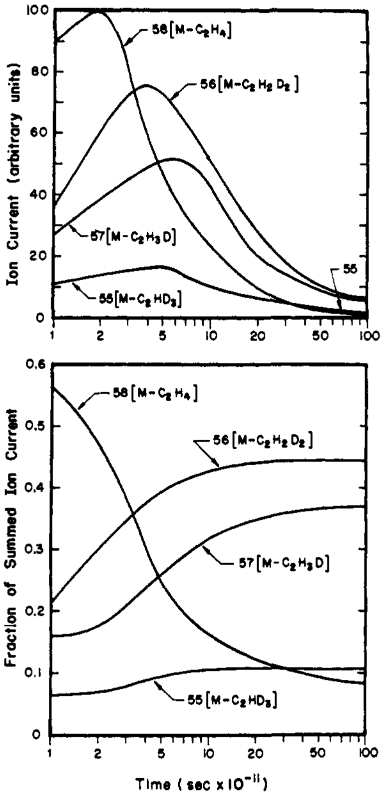

Figure 5. Ion currents $I_f(t)$ due to the fragment ions *m/e* 55, 56, 57, and 58 formed following FI of cyclohexene-*3,3,6,6-d*$_4$ as a function of the molecular ion lifetime. The "summed ion current" referred to in the lower portion of the figure is the sum of the currents of the four ions shown. The ratios of the fractional ion currents at any time are equal to the ratios of the rates of formation of the ions at that time.

The fragment ion currents in Figure 4 represent decompositions occurring in space *between the blade and the cathode.* Some of the structure in the profiles in Figure 2, however, represents decompositions occurring elsewhere in the source. Thus, the maximum in the *m/e* 67 profile at about V_B = 8700 V is attributed to decomposition on the potential plateau ($V_1 = V_F$) between the focus electrodes (see Figure 3). Hence, in constructing the *m/e* 67 curve in Figure 4, only the portion of the *m/e* profile in Figure 2 at V_B < 8600 V has been considered. The maximum at about V_B = 9800 V in *m/e* 67 and those at about V_B = 8200 V in *m/e* 40.5 and 40 are all attributed to decompositions occurring in the field-free region between the ion source exit slit and the entrance to the electric sector.

Curves of ion current $I_f(t)$ against molecular ion lifetime for fragment ions of cyclohexene-*3,3,6,6-d*$_4$, obtained in the same manner as the curves for cyclohexene in Figure 4, are shown in Figures 5–7.

The ion currents $I_f(t)$ appearing in Figures 4–7 represent numbers of ions formed in small finite time intervals Δt of the order of 10^{-11} or 10^{-10} sec. The magnitudes of these intervals are calculated from the energy resolution of the electric sector analyzer, the molecular ion mass, the fragment ion mass, and the molecular ion lifetime.[2b,10] The ion currents $I_f(t)$ are readily con-

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(14) J.-P. Pfeifer, A. M. Falick, and A. L. Burlingame, *Proc. 19th Annu. Conf. Mass Spectrom. Allied Top., 1971,* 52 (1971).

(15) J.-P. Pfeifer, A. M. Falick, and A. L. Burlingame, submitted to *Int. J. Mass Spectrom. Ion Phys.* for publication.

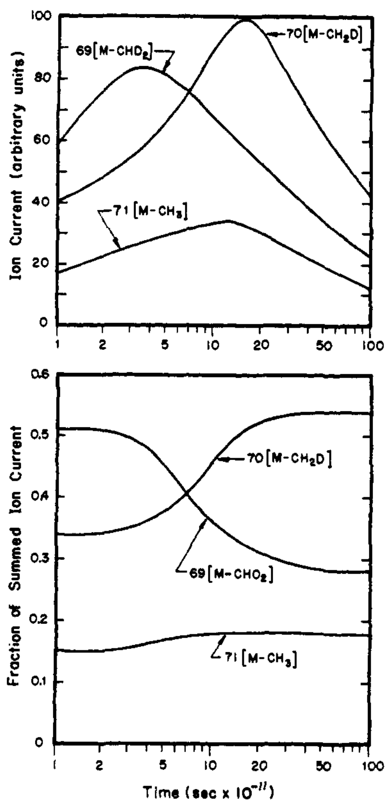

Figure 6. Ion currents $I_f(t)$ due to the fragment ions *m/e* 69, 70, and 71 formed following FI of cyclohexene-*3,3,6,6-d*$_4$ as a function of the molecular ion lifetime. The ratios of the fractional ion currents at any time are equal to the ratios of the rates of formation of the ions at that time.

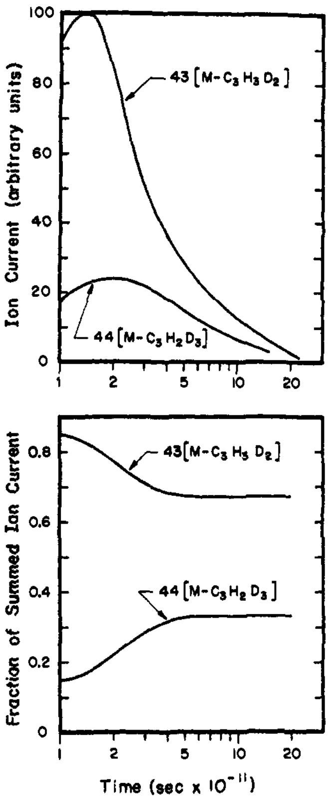

Figure 7. Ion currents $I_f(t)$ due to the fragment ions *m/e* 43 and 44 formed following FI of cyclohexene-*3,3,6,6-d*$_4$ as a function of the molecular ion lifetime. The ratio of the fractional ion currents at any time is equal to the ratio of the rates of formation of the ions at that time.

verted to rates of reaction either by division by these time intervals Δt[2b] or more accurately by deconvolution procedures.[3,4] For the purposes of our discussion, however, conversion of ion currents $I_f(t)$ to rates of reaction is unnecessary, since for fragment ions of similar mass (as in Figures 5–7) the ratios of their currents $I_f(t)$ at any time can be considered to be equal to the ratios of their rates of formation at that time.[2b,10]

The EI mass spectra of cyclohexene and cyclohexene-*3,3,6,6-d*$_4$ at 70-eV and at nominally 12-eV energies are reproduced in Figure 8.

Discussion of Results

(a) Nature of Reactions Induced by FI. There are three principal fragment ions (*m/e* 67, 54, and 41) formed by unimolecular gas-phase reactions induced by FI of cyclohexene. The fragment ions formed in the immediate vicinity of the blade, and hence contributing to the "normal" FI mass spectrum, may originate from reactions in a condensed phase or from surface reactions; however, ions formed in the space between blade and cathode (times $>1 \times 10^{-11}$ sec) are the result of genuine gas-phase reactions. Further, at times of 10^{-11}–10^{-5} sec these gas-phase reactions are not expected to be significantly influenced by interaction with the very high electric field in the immediate vicinity of the blade, since the molecular ion is drawn out of this field within about 2×10^{-11} sec.[10] It is the reactions at 10^{-11}–10^{-5} sec which are of greatest interest for the purposes of our discussion.

m/e **54 (M − C_2H_4)·+.** The formation of the fragment ion *m/e* 54 following FI of cyclohexene is attributed to elimination of ethylene from the molecular ion. Following FI of cyclohexene-*3,3,6,6-d*$_4$, there are four measurable fragment ions *m/e* 58 (M − C_2H_4), 57 (M − C_2H_3D), 56 (M − $C_2H_2D_2$), and 55 (M − C_2HD_3) (Figures 1 and 5) corresponding to *m/e* 54 in cyclohexene. In Figure 5, the *m/e* 57 ion current contains a contribution at short times ($<2 \times 10^{-11}$ sec) from the metastable peak m* 57.0 (86 → 70), and all the ion currents may contain small contributions at times $<2 \times 10^{-11}$ sec from ions equivalent to *m/e* 55 in the unlabeled molecule.

The observation of four ions in the deuterated molecule corresponding to the one ion in cyclohexene indicates that considerable rearrangement of the hydrogens and deuteriums occurs prior to elimination of ethylene. It is evident from Figure 5 that the relative rates of formation of the four ions are sensitive functions of time. We suggest that the dependence of the relative rates of formation upon time reflects the progress of the H–D rearrangements prior to the elimination of ethylene. This being so, careful consideration of the FI results leads to the conclusion that the rearrangement and elimination occur as in Scheme I. The elimination of ethylene is thus postulated to be formally a retro-Diels–Alder (RDA) reaction and the H–D rearrangement a 1,3-allylic rearrangement. It has been suggested previously that the elimination of ethylene from cyclohexene following EI was an RDA reaction,[16–18]

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(16) K. Biemann, "Mass Spectrometry (Organic Chemical Applications)," McGraw-Hill, New York, N. Y., 1962, p 102.

(17) H. Budzikiewicz, J. I. Braumann, and C. Djerassi, *Tetrahedron*, 21, 1855 (1965).

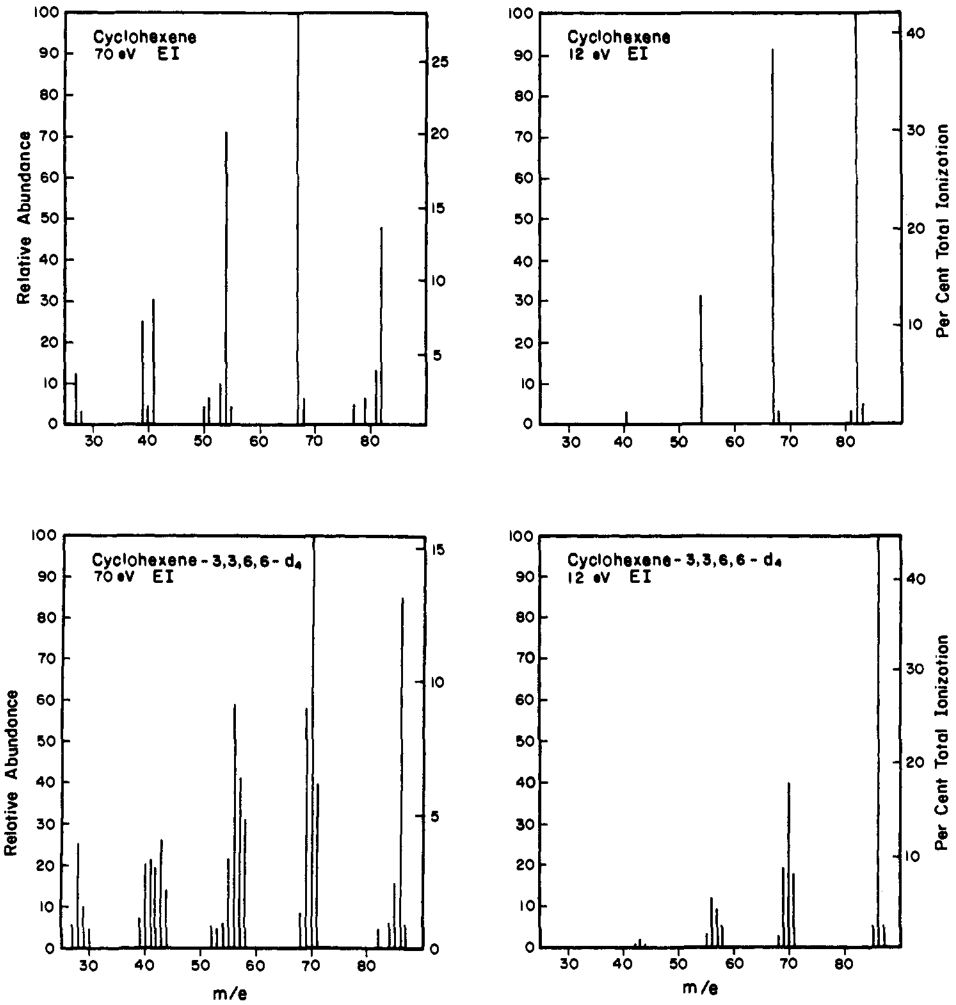
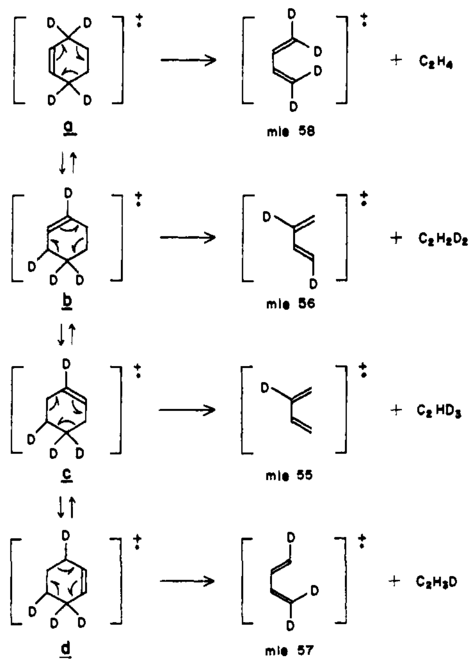


Figure 8. EI mass spectra of cyclohexene and cyclohexene-*3,3,6,6-d_4* at 70 eV and nominally 12-eV ionizing electron energies.

and 1,3-allylic rearrangements have been invoked to account for the H–D randomization induced by EI of $\Delta^{4(8)}$-menthene[19] and methylcyclohexene.[20] The evidence upon which these earlier suggestions was based was, however, rather tenuous.

Considering Scheme I in more detail, the unrearranged molecular ion a on undergoing an RDA reaction yields the fragment *m/e* 58 $(M - C_2H_4)\cdot^+$, hence explaining the importance of this ion at the shortest times and its steady decline with time. The ion current of *m/e* 58 at 1×10^{-9} sec is equal within experimental error to the value calculated assuming complete randomization of H and D (Table I). The molecular ion b formed by one allylic rearrangement reacts to give *m/e* 56 $(M - C_2H_2D_2)\cdot^+$ (Scheme I). This is consistent with the rapid rise in the relative rate of formation of *m/e* 56 at the shortest times (Figure 5). The maximum for the *m/e* 56 ion current $I_t(t)$ occurs at a longer time than that for *m/e* 58, but at a shorter time than those for *m/e* 55 and 57 (Figure 5). The formation of the fragment *m/e* 55 requires that at least two successive allylic rearrangements occur prior to elimination of ethylene, and the formation of *m/e* 57 requires at least three successive rearrangements (Scheme I). It is thus satisfactory that the maximum in the *m/e* 55 ion current $I_t(t)$ curve occurs at a slightly shorter time than that in the *m/e* 57 curve (Figure 5).

Scheme I



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(18) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, p 67.

(19) D. S. Weinberg and C. Djerassi, *J. Org. Chem.*, 31, 115 (1966).

(20) T. H. Kinstle and R. E. Stark, *ibid.*, 32, 1318 (1967).

Table I. The Observed and Calculated Relative Ion Currents of Fragment Ions Formed by Loss of Ethylene from Ionized Cyclohexene-*3,3,6,6*-d_4

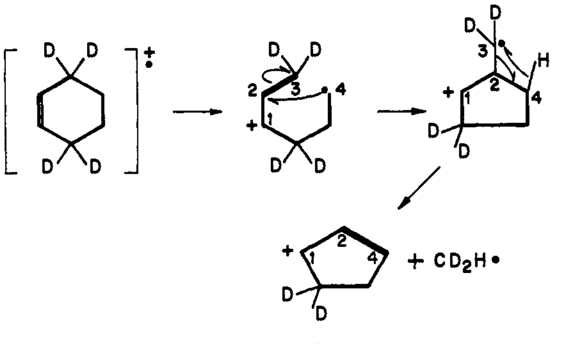
	m/e			
	55	56	57	58
Theoretical (assuming complete H–D randomization)	12	43	38	7
Field ionization				
1×10^{-11} sec	7	21	16	56
1×10^{-10} sec	10	42	32	16
1×10^{-9} sec	11	44	37	8
Electron impact				
70 eV	14	37	27	22
Nominally 12 eV	12	40	32	17

The 1,3-allylic rearrangements occur in times of 10^{-12}–10^{-11} sec since the proportion of *m/e* 58 is falling rapidly even at 1×10^{-11} sec (Figure 5). The hydrogens and deuteriums are close to complete randomization after 1×10^{-10} sec and are completely randomized after 1×10^{-9} sec (Table I). There is apparently no significant isotope effect in these rearrangements. If the 1,3-allylic rearrangement is assumed to be a sigmatropic reaction, the orbital symmetry rules of Woodward and Hoffmann predict that the migration occurs antarafacially.[21]

m/e **67** $(M - CH_3)^+$. The formation of the fragment ion *m/e* 67 (Figures 1 and 4) following FI of cyclohexene is interpreted as loss of a methyl radical from the molecular ion. Following FI of cyclohexene-*3,3,6,6*-d_4, there are three measurable fragment ions *m/e* 71 $(M - CH_3)^+$, 70 $(M - CH_2D)^+$, and 69 $(M - CHD_2)^+$ (Figures 1 and 6) corresponding to *m/e* 67 in cyclohexene. Again the relative rates of formation of the three ions are functions of time (Figure 6). Their dependence on time is certainly due at least in part to the 1,3-allylic rearrangements within the molecular ion (Scheme I).

It is reasonable to assume that the first step in the loss of a methyl radical from cyclohexene is an allylic cleavage to form a straight chain structure.[17,18] Hydrogen transfer to a terminal carbon followed by, or concurrent with, C–C bond cleavage can then yield the $(M - CH_3)^+$ ion. The most plausible mechanism for the transfer would appear to be hydrogen migration from C-6 to C-4, since on expelling C-4 as the methyl radical a conjugated pentadiene ion would be formed.[17,18] The FI results do not, however, support this mechanism. The predominant fragment ion at the shortest times is *m/e* 69 $(M - CHD_2)^+$ (Figure 6), suggesting that this is the fragment formed from the cyclohexene-*3,3,6,6*-d_4 ion, in which case the major process for the loss of a methyl radical from the cyclohexene-*3,3,6,6*-d_4 ion effects the elimination of C-3, rather than C-4. A possible mechanism is shown in Scheme II. Such a ring-contraction mechanism is energetically feasible by virtue of the stable cyclopentene ion predicted to be formed. Closely analogous ring-contraction mechanisms have been proposed for the EI-induced fragmentation of acylated cyclic amines.[22,23]

Scheme II



The relative ion currents of *m/e* 69, 70, and 71 at various times after FI of cyclohexene-*3,3,6,6*-d_4 are shown in Table II. At all times after 1×10^{-9} sec the measured values are very close to those calculated assuming random loss of H and D. The small observed differences may reflect primary isotope effects.

Table II. The Observed and Calculated Ion Currents of Fragment Ions Formed by Loss of a Methyl Group from Ionized Cyclohexene-*3,3,6,6*-d_4

	m/e		
	69	70	71
Theoretical (assuming complete H–D randomization)	30	48	22
Field ionization			
1×10^{-11} sec	51	34	15
1×10^{-10} sec	36	46	18
1×10^{-9} sec	28	54	18
At focus electrodes (4×10^{-8} sec)	26	54	20
Metastables in first field-free region (10^{-7}–10^{-6} sec)	27	51	22
Metastables in second field-free region (10^{-5} sec)	27	50[a]	23
Electron impact			
70 eV	29	51	20
Nominally 12 eV	24	51	25

[a] Assumed value since m* (86 → 70) is coincident with *m/e* 57 $(M - C_2H_3D)$.

m/e **40,** *m/e* **40.5, and** *m/e* **41.** The FI ion current–blade potential profiles of *m/e* 40 and 40.5 in cyclohexene are interesting because of the maxima at around 8200 V (see Figure 2), which we interpret as arising from transitions in the field-free region between the ion source and the electric sector (*i.e.*, at 10^{-7}–10^{-6} sec)

$$C_6H_{10}^{2+} \longrightarrow C_6H_8^{2+} + H_2$$

$$C_6H_{11}^{2+} \longrightarrow C_6H_9^{2+} + H_2$$

The FI results with cyclohexene-*3,3,6,6*-d_4 support these interpretations. The formation of doubly charged ions by FI of unsaturated cyclic hydrocarbons is well established.[24-27] Decompositions of doubly charged ions to yield other doubly charged ions have been reported previously.[28,29] Moreover, elimination of a

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(21) K. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1971, p 114.

(22) W. J. Richter, J. M. Tesarek, and A. L. Burlingame, *Org. Mass Spectrom.*, **5**, 531 (1971).

(23) W. J. Richter, J. M. Bursey, and A. L. Burlingame, *ibid.*, **5**, 1295 (1971).

(24) H. D. Beckey in "Mass Spectrometry," R. I. Reed, Ed., Academic Press, New York, N. Y., p 39.

(25) I. Z. Korostishevsky and I. V. Goldenfeld, *Prib. Tekh. Eksp.*, **1**, 146 (1968).

(26) V. A. Nazarenko, I. V. Goldenfeld, and P. S. Dibrova, *Int. J. Mass Spectrom. Ion Phys.*, **2**, 92 (1969).

(27) See ref 2b, p 268.

(28) S. Meyerson and W. Vander Maar, *J. Chem. Phys.*, **37**, 2458 (1962).

(29) P. Schulze and A. L. Burlingame, *ibid.*, **49**, 4870 (1968).

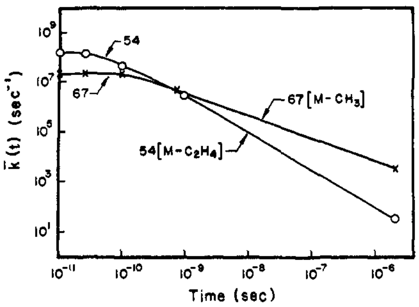


Figure 9. The average rate constant $\bar{k}(t)$ as a function of time for the formation of m/e 54 and 67 from cyclohexene following FI.

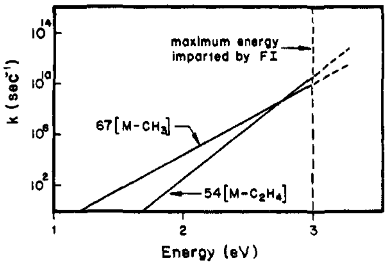


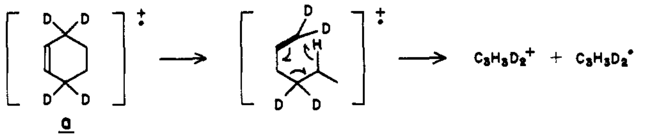
Figure 10. Schematic curves of the microscopic rate constant k as a function of internal excitation energy for the formation of m/e 54 and 67 from cyclohexene following FI.

hydrogen molecule is a common decomposition of this type in phenetole and cyclic amines.[29] The ion current of m/e 40 at V_B = 8000–8100 (Figure 2) is interpreted as $C_3H_4^+$ formed by field dissociation.[30]

The FI ion current of m/e 41 in cyclohexene is mainly due to $(M - C_3H_5)^+$. At the shortest times ($\sim 1 \times 10^{-11}$ sec) there is probably a contribution from $C_6H_{10}^{2+}$. The doubly charged ion will not, however, be formed beyond the immediate vicinity of the blade. Following FI of cyclohexene-*3,3,6,6-d*$_4$, there are two measurable ions m/e 43 $(M - C_3H_3D_2)^+$ and m/e 44 $(M - C_3H_2D_3)^+$ (Figures 1 and 7) corresponding to m/e 41 in cyclohexene. The fragment ion m/e 42 $(M - C_3H_4D^+)$ is also detected, but cannot be measured sufficiently accurately because of the presence of $C_3H_2D_2^+$ at V_B = 8000–8100 V and $C_6H_4D_4^{2+}$ at $V_B \sim 8200$ V.

It appears from Figure 7 that m/e 43 $(M - C_3H_3D_2)^+$ is formed from the cyclohexene-*3,3,6,6-d*$_4$ ion. This conclusion needs, however, to be treated with some reservation, since the influence of double charged ions $C_6H_6D_4^{2+}$ on the results cannot be accurately assessed. A possible mechanism for the formation of m/e 43 $(M - C_3H_3D_2)^+$ is shown in Scheme III.

Scheme III



Kinetics of the Formation of *m/e* 54 $(M - C_2H_4)\cdot^+$ and *m/e* 67 $(M - CH_3)^+$ Following FI of Cyclohexene. An average rate constant $\bar{k}(t)$ for the formation of a fragment ion following FI of cyclohexene can be defined as follows[2]

$$\bar{k}(t) = \{I_f(t)/I_M(t)\Delta t = I_f(t)/I_M\Delta t$$

$I_f(t)$ and Δt have been discussed earlier. $I_M(t)$ is the total ion current of undecomposed cyclohexene ions M^+ at time t. It is, however, acceptable for the purposes of our discussion to replace $I_M(t)$ by the ion current I_M of M^+ in the "normal" FI mass spectrum. The calculated rate constants $\bar{k}(t)$ for the formation of m/e 54 and 67 are displayed in Figure 9. The points in Figure 9 from 1×10^{-11} to 1×10^{-9} sec are based on Figure 4. The points at 1×10^{-6} sec are based on measurements of metastable transitions in the field-free region between the ion source and the electric sector.[31]

It is apparent from Figure 9 that $\bar{k}(t)$ for m/e 54 is approximately 10 times *greater* than that for m/e 67 at 1×10^{-11} sec, but is approximately 100 times *smaller* than that for m/e 67 at 1×10^{-6} sec. The rate constants $\bar{k}(t)$ for the two processes are equal at a time slightly shorter than 1×10^{-9} sec.

The average rate constant $\bar{k}(t)$ is an experimental quantity, describing the reaction of a sample of molecules possessing a *range* of internal excitation energies E. For theoretical considerations, however, it is desirable to know the rate constant k for a sample of molecules all of which possess the same discrete amount of internal excitation energy. The relationship between $\bar{k}(t)$ and k is thus analogous to that between the phenomenological and microscopic cross sections of an ion–molecule reaction. In order to make a clear distinction between k and $\bar{k}(t)$, we shall where necessary refer to k as the "microscopic rate constant." The derivation of k from $\bar{k}(t)$ demands a precise knowledge of the distribution of internal excitation energy E imparted to a molecule during FI, which at the present time is not available.

The form of the curves of $\bar{k}(t)$ against time (Figure 9) does, however, give some indication as to the most probable form of the curves of k against E for the processes forming m/e 54 and 67. The *initial* distribution of internal excitation energy available for reaction is the same for both processes. Assuming that the basic tenets of the quasiequilibrium theory[32,33] are valid and that the curves of k against E are smooth at the low energies involved, the intersection in the curves of $\bar{k}(t)$ against time suggests that the curves of k against E also intersect in the manner shown schematically in Figure 10. The maximum energy available for ionization by FI with a blade emitter is generally assumed to be about 12 eV. Hence, since the lowest ionization potential of cyclohexene is about 8.9 eV, the maximum internal excitation energy is about 3 eV.

The higher average rate constants $\bar{k}(t)$ for m/e 54 at the shortest times ($\sim 10^{-11}$ sec) suggest that the microscopic rate constants k contributing to the rates of reaction at these times are also higher for m/e 54 than for m/e 67. The most energetic ions react at the shortest times, so that at the highest values of the internal excitation energy E the microscopic rate constants k for m/e 54 are probably higher than those for m/e 67. This being so, the conclusion that the curves of k against E intersect follows from the fact that EI mea-

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surements of appearance potentials[17,34] indicate that the activation energy for the formation of m/e 54 is probably about 0.5 eV higher than that for the formation of m/e 67. Further, the shallower slope of the proposed curve of k against E for m/e 67 can satisfactorily explain the shallower slope of the $\bar{k}(t)$ against time curve for m/e 67.

The curves of $\bar{k}(t)$ against time contain another feature to be discussed, which is that at the shortest times $\bar{k}(t)$ is approximately independent of time (Figure 9). The times at which $\bar{k}(t)$ begins to show time dependency coincide with the times of the maxima in the fragment ion currents $I_f(t)$ (Figure 4). Beckey and his colleagues[35,36] have observed similar behavior in FI studies of other molecules. The formation of m/e 67 probably involves several steps, hence the time independent $\bar{k}(t)$ may reflect the kinetics of the consecutive reactions. Such an explanation is, however, less likely for the formation of m/e 54. An alternative explanation has been offered by Beckey and his colleagues[35-37] who claim that, although a distribution of microscopic rate constants k is necessary for an adequate description of an FI reaction over the whole time range 10^{-11}–10^{-5} sec, a reaction can be effectively described by just the maximum $k_{\max}$ in the distribution at all times $<1/k_{\max}$, in which case $\bar{k}(t)$ will be observed to be independent of time at times $<1/k_{\max}$. According to this explanation, therefore, the times at which the $\bar{k}(t)$ in Figure 9 begin to show time dependency represent $1/k_{\max}$, so that $k_{\max}$ would be 3×10^{10} sec^{-1} for m/e 54 and 1×10^{10} sec^{-1} for m/e 67. These figures support the k *vs.* E curves proposed for the two reactions.

It is interesting to note that the formation of m/e 54 involves only direct bond dissociations, whereas the formation of m/e 67 involves intramolecular rearrangement. The proposed intersection of the k *vs.* E curves may, therefore, indicate that the formation of m/e 67 possesses not only the lower activation energy but also the lower frequency factor.[38,39]

(b) Comparison of the EI Mass Spectra of Cyclohexene and Cyclohexene-*3,3,6,6-d*$_4$ with the FI Results. The same fragment masses, m/e 67 $(M - CH_3)^+$, 54 $(M - C_2H_4)^+$, and 41 $(M - C_3H_5)^+$, are formed from cyclohexene following low-energy (nominally 12 eV) EI (Figure 8) as are formed at 10^{-11}–10^{-5} sec following FI. The fragment ion currents in the low-energy EI mass spectrum represent the total numbers of ions formed within some time interval of the order of 10^{-6} sec. In order to make any quantitative comparison between the degrees of fragmentation in EI and FI, it is necessary to estimate the numbers of fragment ions I_f formed within the same interval following FI. Fragment ions formed within the very high electric field at 10^{-14}–10^{-12} sec can, however, be neglected without introducing significant error. The estimations of I_f have, therefore, been performed by integrating $\bar{k}(t)$ from 10^{-11} to 5×10^{-6} sec (see relationship 2) after approximating each of the $\bar{k}(t)$ against time curves in Figure 9 to two straight lines.

$$I_f = \int_{10^{-11}}^{5 \times 10^{-6}} \frac{dI_f}{dt}\,dt = \int_{10^{-11}}^{5 \times 10^{-6}} I_M(t)\bar{k}(t)\,dt = I_M \int_{10^{-11}}^{5 \times 10^{-6}} \bar{k}(t)\,dt \quad (2)$$

Thus, for example, the m/e 67 curve has been considered for the purposes of integration as a straight line parallel to the x axis from 10^{-11} to $10^{-10.3}$ sec and as a straight line of slope -0.95 from $10^{-10.3}$ to 10^{-6} sec. The results of the integrations indicate that the fraction of m/e 67 ions formed from 10^{-11} to 5×10^{-6} sec is 0.05 relative to I_M and that the fraction of m/e 54 ions is 0.02. The comparable figures for the low-energy EI spectrum are 0.91 and 0.31, respectively.

The possible errors in the calculated figures for I_f are unlikely to affect the order of magnitude of the results. It can, therefore, be concluded that the degree of fragmentation following FI with a blade emitter at 100° is an order of magnitude less than that following nominally 12-eV EI at 180°. This difference in the extent of fragmentation can be safely attributed to a greater average amount of internal excitation energy being imparted to the molecule with the nominally 12-eV EI.

It is evident from the EI mass spectra of cyclohexene-*3,3,6,6-d*$_4$ (Figure 8) that extensive H–D randomization occurs prior to fragmentation. The observed ion currents of fragment ions formed after EI by loss of a methyl radical (Table II) conform very closely to the figures calculated assuming complete randomization of H and D, whereas the observed ion currents of fragment ions formed by loss of ethylene (Table I) deviate significantly from the calculated figures. This contrast as to the degrees of H–D randomization cannot be satisfactorily explained by primary or secondary isotope effects. The contrast at least in the low-energy EI spectrum is, however, explained if it is assumed that the natures of the reactions are essentially similar following low-energy EI and following FI at 10^{-11}–10^{-5} sec. Making this assumption, the FI results indicate that at low energies H–D randomization is complete within 1×10^{-9} sec. At times less than about 1×10^{-9} sec and prior to complete randomization, the loss of ethylene is the predominant fragmentation reaction at low energies. At times greater than about 1×10^{-9} sec, however, when H and D are completely randomized, the loss of a methyl radical becomes the predominant fragmentation reaction. It is, therefore, to be expected that in the low-energy EI mass spectra of cyclohexene-*3,3,6,6-d*$_4$ H–D randomization should be more strongly manifested in the loss of a methyl radical than in the loss of ethylene. It is reasonable that the ion current of the fragment ion m/e 58 formed by loss of ethylene from the unrearranged cyclohexene-*3,3,6,6-d*$_4$ ion (Scheme I) should be enhanced over the theoretical value (Table I), since the loss of ethylene can occur to a significant degree prior to the allylic rearrangements effecting H–D randomization. It seems probable that the above explanation is also equally valid for the 70-eV EI results.

The relative ion currents of m/e 58 and 69 in the EI mass spectra of cyclohexene-*3,3,6,6-d*$_4$ both increase slightly on raising the electron energy (Tables I and II).

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These are the fragment ions formed from the unrearranged cyclohexene-*3,3,6,6-d_4* ion, assuming that the mechanisms in Schemes I and II are valid for the reactions induced by EI. The increased ion currents may, therefore, indicate that, as might be expected,[38,39] on raising the electron energy the rates of the fragmentation reactions are enhanced to a greater degree than the rates of the allylic rearrangements effecting H–D randomization.

Conclusion

The same reactions of cylohexene appear to be induced by FI at 10^{-11}–10^{-5} sec and by nominally 12-eV EI, although the amount of internal excitation energy is somewhat greater in the case of EI. The same H–D rearrangements appear to be induced in cyclohexene-*3,3,6,6-d_4* by both EI and FI. The reactions induced by FI should not be significantly influenced by external electric fields at times $>2 \times 10^{-11}$ sec. We, therefore, conclude that with cyclohexene and cyclohexene-*3,3,6,6-d_4* the reactions induced by low-energy (nominally 12 eV) EI are probably essentially similar in nature to the reactions occurring at 10^{-11}–10^{-5} sec following FI. Major differences are likely to be limited to reaction rates being somewhat more rapid following EI due to greater internal excitation energies.

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Gas- and Liquid-Phase Oxidations of *n*-Butane

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Abstract: The rates and products of *t*-Bu_2O_2-initiated oxidations of *n*-butane have been studied in the gas and liquid phase at 100 and 125°. After allowance for concentration changes, effects of phase change at 125° are surprisingly small. In neat liquid butane at 125°, yields of hydroperoxide are as high as 77% at low rates of initiation. As the rate of initiation increases and as the concentration of butane decreases, yields of *sec*-butyl alcohol and methyl ethyl ketone (chain termination products) and of ethanol and acetaldehyde (cleavage products of *sec*-BuO· radicals) increase, and kinetic chain lengths decrease. With 0.044 *M* butane in the gas phase, less than 0.5 molecule of butane is consumed per initiating *t*-BuO· radical, and oxidation of methyl radicals (from *t*-BuO· radicals) accounts for much of the oxygen consumed. The methyl and ethyl (peroxy) radicals from cleavage of *t*-BuO· and *sec*-BuO· radicals complicate determinations of some important ratios of rate constant, but we estimate that 50–70% of the interactions of *sec*-BuO_2· radicals are nonterminating (in either phase). The ratio of cleavage to propagation for *sec*-BuO· radicals measured in separate experiments is about eight times as large as for *t*-BuO· radicals in the liquid phase and significantly larger than estimated from oxidation experiments. From the ratio of *sec*-BuOH to *n*-BuOH formed, we calculate that the relative reactivities of the secondary and primary C–H bonds for attack by peroxy radicals at 100° is about 45:1.

Earlier fundamental studies of autoxidations of hydrocarbons have been concerned with liquid-phase oxidations below 100°, gas-phase oxidations about 250°, and reactions of alkyl radicals with oxygen in the gas phase at 25°. In a previous investigation of the transitions between these three regions, we studied the rates and products of oxidation of isobutane[2] between 50 and 155°. We now have extended that investigation to *n*-butane in order to determine the effects of temperature, concentration, and phase change on the rates and products of oxidation of *n*-butane, to establish the most important elementary steps, and to compare the oxidations of *n*-butane and isobutane.

Experimental Section

Materials. Oxygen (Matheson) and *n*-butane (Phillips) were research grade gases. Di-*tert*-butyl peroxide (Lucidol) was distilled under vacuum; no *tert*-butyl alcohol or acetone was detected by glpc. We prepared *sec*-Bu_2O_2 in 98% purity by the procedure of Mosher, *et al.*[3]

Procedures. The equipment, techniques, and procedures used for this work were similar to those used previously for isobutane[2] except for the analyses of neat *n*-butane.

When benzene was used as a solvent, it was first weighed into the reaction flask. *n*-Butane, measured in a larger calibrated vessel and introduced into this flask through a capillary side arm and stopcock, was frozen, and a known amount of oxygen was forced into the flask with a Toepler pump. Initiator from a tared microliter syringe was then injected through another capillary side arm fitted with a serum cap. After the flask was charged, both capillary arms were sealed off, and the flask was immersed in a constant temperature bath. During liquid-phase runs, the vessel was shaken with a Burrell wrist-action shaker. Oxidation was stopped by quickly cooling the flask to room temperature.

Analyses. Analyses on noncondensable gases were carried out by the same procedures used in isobutane experiments,[2] using a Cu–CuO combustion furnace coupled to a gas buret. Mixtures of CO and H_2 from *sec*-Bu_2O_2 experiments were analyzed by mass

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