quent trapping with various reagents. Thus far there have been no literature reports of experiments of this nature. However, it can be said that synthetic procedures are now at hand to make such studies imminent. Our own work has progressed to the point where pentalene complexes can be obtained in 30% yields, making 200–300-mg quantities readily available, and attention is now directed to such investigations. It should be appreciated, however, that with these complexes the pentalenes comprise a relatively small fraction of the total weight of complex, so that progress in this direction is perhaps likely to be slow.

Kinetics and Mechanisms of Unimolecular Gas-Phase Reactions of Radical Cations at Times of 10^{-11} to 10^{-5} Sec Following Field Ionization[1]

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Received November 26, 1973

Field ionization (FI) is the removal of an electron from an organic molecule in the gas phase through interaction with a very strong field (10^9–10^{10} V/m). The radical cations are produced with sufficient vibrational energy to undergo a rich variety of competing unimolecular chemical reactions.[2,3] The reactions are rapid, often occurring in times comparable to periods of molecular vibrations, and complex molecular rearrangements occur in times as short as picoseconds. Such unimolecular gas-phase reactions of radical cations are intimately and inextricably linked with mass spectrometry. Regrettably the close association has sometimes resulted in the intrinsic chemistry of these reactions being overlooked in the face of the analyst's pragmatic views that the reactions are merely the means of producing a mass spectrum. The characteristically fast rates of the reactions, so essential to the effectiveness of mass spectrometry as an analytical technique,[4] pose problems when the object is to elucidate the kinetics.

Electron-impact (EI) mass spectrometry affords an integrated view of all reaction occurring within a few *microseconds* of ionization but, of course, precludes the possibility of obtaining kinetic data on reactions taking place in less than microseconds.[5,6] Sequential rearrangements each occurring in picoseconds appear bewilderingly complex when viewed after microseconds, so that it becomes impossible even to identify

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(1) The experimental work described was performed at the Space Sciences Laboratory, University of California, Berkeley, in collaboration with Dr. A. M. Falick.

(2) (a) F. M. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, New York, N.Y., 1957; (b) J. H. Beynon, "Mass Spectrometry and Its Applications to Organic Chemistry," Elsevier, Amsterdam, 1960; (c) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967; (d) F. W. McLafferty in "Topics in Organic Mass Spectrometry," A. L. Burlingame, Ed., Wiley-Interscience, New York, N.Y., 1970.

(3) (a) P. Bommer and K. Biemann, *Annu. Rev. Phys. Chem.,* 16, 481 (1965); (b) I. Howe in "Mass Spectrometry," Volume 2, D. H. Williams, Senior Reporter, The Chemical Society, London, 1973; (c) F. P. Boer, T. W. Shannon, and F. W. McLafferty, *J. Amer. Chem. Soc.,* 90, 7239 (1968).

(4) The mass spectrum displays those product ions formed within the ionizing chamber before the ions are extracted into the ion gun. In an electron-impact (EI) mass spectrometer, ions typically reside within the ionizing chamber for microseconds. Due to the very fast rates, the reaction systems initiated by ionization typically proceed almost to completion well within such times. The mass spectrum is thus approximately independent of the precise time the ions reside within the ionizing chamber. It is important that this be so, since residence times within the source do vary from instrument to instrument. A strong dependence of the mass spectral composition on residence time could mean that the mass spectrum of a given compound would not be a standard reproducible characteristic.

(5) Using specialized EI mass spectrometric techniques, C. Ottinger and his colleagues [*Z. Naturforsch. A,* 22, 20 (1967)] and V. L. Tal'roze and his colleagues [*Kinet. Katal.,* 8, 1 (1967)] have been able to measure lifetimes in the nanosecond time frame.

(6) Ion cyclotron resonance provides data at times of the order of milliseconds. See, for example, J. D. Baldeschwieler, *Science,* 159, 263 (1963).

Razor Blade at High Positive Potential (8–10 kV)

Ionization Region at Apex

Decomposition Region for Reaction Times from 10^{-12} sec to 10^{-8} sec

1/4 mm

Reactant Ions' Trajectory

Ion Lens and Mass Spectrometer to Identify Reaction Products and to Measure their Kinetic Energy Distributions
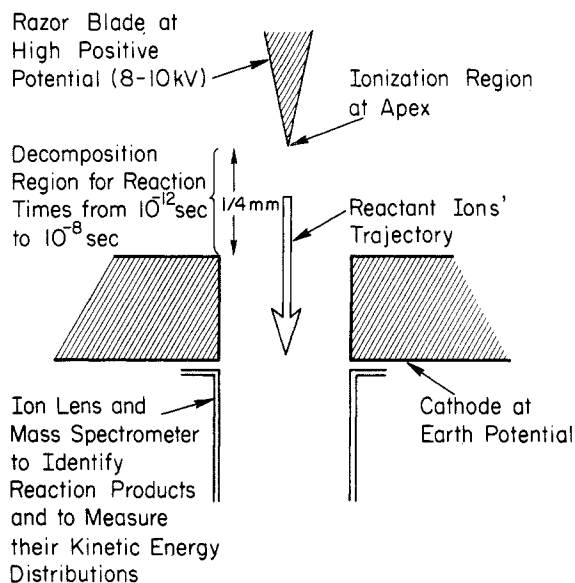
Cathode at Earth Potential

Figure 1. The reaction vessel.

the individual processes. This is particularly true with regard to rearrangements effecting isotopic randomization (*vide infra*). The field ionization kinetics (FIK) technique[7] yields the necessary information to identify qualitatively the nature of the competing reactions in the picosecond time frame and in addition allows the course of each reaction to be followed down into the microsecond time frame.[8] Reaction rates and phenomenological rate constants are accessible over seven orders of magnitude of time from 10^{-12} sec to 10^{-5} sec.[9-13]

The Field Ionization Kinetics (FIK) Technique

The strong fields necessary for FI are realized at the surfaces of highly curved electrodes raised to high positive potentials with respect to a proximate cathode[14-16] (Figure 1). In these experiments the highly curved electrodes are commercial razor blades.[16,17] Ionization occurs only in a very small region of the order of 100 Å in depth at the blade edge. The radical cations so formed are referred to as molecular ions and are the activated molecules whose reactions are to be studied. The assemblies of molecular ions formed by FI possess *distributions of internal energy E*. A typical distribution might have its mean in the region of tenths of an electron volt (in the region of kilocalories) and extend over several

electron volts (tens of kilocalories).[11,18] The exact form of the distribution is not reliably known for any molecule. The degree of reaction induced by FI is often comparable to that induced by 10–12-eV electrons in EI techniques.

Following FI, the molecular ions are accelerated away from the blade toward the cathode by the electric field (Figure 1). Consider a molecular ion which decomposes in the potential gradient between the blade and the cathode. The kinetic energy (eV) of the ionic product on reaching ground potential can be expressed as[12,13]

$$eV = eV_1 + \frac{em}{M}(V_B - V_1) \tag{1}$$

V_B and V_1 are the potentials at the blade and at the position where decomposition occurs, respectively; M and m are the masses of singly charged molecular and product ion, respectively; and e is the charge of an electron. Expression 1 relates the kinetic energy eV to the potential V_1 at the position where decomposition occurs. The flight time of the molecular ion from the blade to the potential V_1 can be calculated,[13,19,20] and can be considered to be the lifetime of the molecular ion prior to decomposition, *i.e.*, the reaction time. In reality the product ions possess a distribution of kinetic energy, arising from a distribution of reaction times, which is measured with a mass spectrometer.

Experimental results take the form of curves of product ion current $I_p(t)$ against kinetic energy, which are transformed according to the principles outlined above to curves of product ion current $I_p(t)$ against reaction time t. The product ion current $I_p(t)$ is related to the rate of reaction dI_p/dt by the expression[9-11,13,16]

$$\frac{dI_p}{dt} = \frac{I_p(t)}{\Delta t} \tag{2}$$

and to a phenomenological rate constant $\bar{k}(t)$ by the expression[9-11,13,16]

$$\bar{k}(t) = \frac{I_p(t)}{\Delta t I_M(t)} \tag{3}$$

Δt is a small interval within which the product ions contributing to the measured product ion current $I_p(t)$ at time t are formed;[13,16] Δt is dependent on the molecular and product ion masses and on the reaction time t. $I_M(t)$ is the ion current of undecomposed molecular ions at time t. The phenomenological rate constant $\bar{k}(t)$ is an experimental quantity describing the real situation in which the assembly of reactants possesses a distribution of internal energy $P(E)$. In contrast, the microscopic rate constant $k(E)$ is a theoretical quantity describing the ideal situation in which reactants possess a discrete amount of internal energy, E (*vide infra*). The procedure outlined above yields reaction times up to 10^{-8} sec. In the present experiments the optimum time resolution is typically a few $\times$ 10^{-11} sec; resolutions of a few picoseconds have, however, been achieved with blade emitters.[12] Kinetic data at 10^{-6} sec and 10^{-5} sec are obtained from measurement of metasta-

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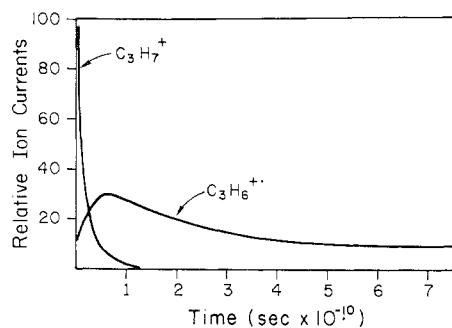(17) A. J. B. Robertson and B. W. Viney, *J. Chem. Soc. A*, 1843 (1966).

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Figure 2. The formation of the products $C_3H_7^+$ and $C_3H_6\cdot^+$ from the 2-methylpropane radical cation $C_4H_{10}\cdot^+$ as a function of time.

ble transitions in the first and second field-free regions of the mass spectrometer.[13]

Dependence of Reactivity upon Time

The most remarkable general observation resulting from FIK experiments is the enormous dependence of the nature of reaction upon time. A molecular ion typically undergoes different reactions in different time frames. Consider the behavior of 2-methylpropane.[21] The radical cation formed by FI reacts to form $C_3H_7^+$ and $C_3H_6\cdot^+$. The formation of $C_3H_7^+$ is seen as a simple bond cleavage to give the stable *sec*-propyl ion.[21-23] Deuterium labeling[21] indicates that the formation of $C_3H_6\cdot^+$ occurs *via* 1,3 hydrogen shifts. The activation energy for formation of $C_3H_7^+$ is probably higher than that for formation of $C_3H_6\cdot^+$ by at least a few tenths of an electron volt (~10 kcal/mol).[24] Figure 2 shows the curves of the product ion currents $C_3H_7^+$ and $C_3H_6\cdot^+$ against time. The ion currents are related to the rates of reaction by expression 2. Since Δt at any particular time will be approximately the same for both reactions,[13] the ratio of the ion currents $C_3H_7^+$ and $C_3H_6\cdot^+$ at any particular time represents the ratio of the rates of reaction at that time. At times of the order of 10^{-11} sec, the rate of formation of $C_3H_7^+$ increases relative to the rate of formation of $C_3H_6\cdot^+$ as time decreases.[25] The formation of $C_3H_6\cdot^+$ predominates at times of the order of 10^{-10} sec. We assume[26] that internal energy is randomized within 10^{-11} sec. The most energetic molecular ions must react at the shortest times and hence the FIK results (Figure 2) tell us that the most energetic ions react to form $C_3H_7^+$ (Figure 2); less energetic ions react at the longer times to form $C_3H_6\cdot^+$.

The results are consistent with the statistical theory of unimolecular reactions, which in mass spectrometry is known as the quasi-equilibrium theory

(QET).[27,28] The theory provides expression 4 for the

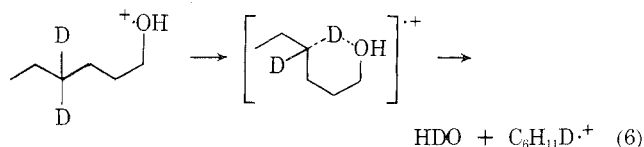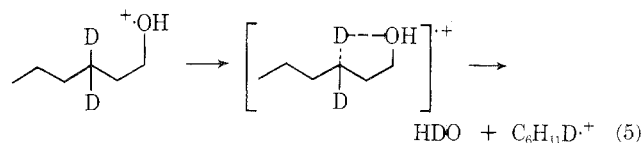$$k(E) = \frac{\sigma G^*(E - E_0)}{hN(E)} \tag{4}$$

dependence of microscopic rate constant $k(E)$ on internal energy E. $G^*(E - E_0)$ is the *total* number of quantum states of the transition state in the energy interval between E and the activation energy E_0; $N(E)$ is the density of states of the reactant at energy E; and σ is a symmetry number. The relative values of the rate constants $k(E)$ for $C_3H_7^+$ and $C_3H_6\cdot^+$ depend on the values of $G^*(E - E_0)$ in the expressions for the two reactions, since the denominator will be identical for either reaction.

For the purposes of our qualitative discussion, we will view $G^*(E - E_0)$ as depending on the *magnitude* of the energy interval $E - E_0$ and on the average density of states within that interval. The energy interval for the formation of $C_3H_6\cdot^+$ will be greater than that for the formation of $C_3H_7^+$ by an amount equal to the difference in their activation energies, $E_0(C_3H_7^+) - E_0(C_3H_6\cdot^+)$. The density of states will, however, be greater for the formation of $C_3H_7^+$. Consideration of rotations shows this to be the case.[26] The direct bond cleavage to form $C_3H_7^+$ need not restrict the internal rotations of the methyls; the transition state may even gain additional rotations, *i.e.*, may be "loose" in the sense of Gorin.[29] Formation of $C_3H_6\cdot^+$ through a 1,3 shift would restrict two internal rotations in the transition state.

The simple model gives a clear physical picture. FI produces molecular ions with a distribution of internal energies, and this distribution changes in time. The most energetic species undergo a simple cleavage. This reaction has a higher energy of activation than the other, but it is still the favored path because of the higher density of states associated with it. Once the most energetic species have reacted by the cleavage mechanism, the remaining molecular ions contain only enough energy to react by the 1,3-shift mechanism. This reaction is slower because the shift restricts the number of accessible states.

Cyclic Transition States

FIK results[30] for processes 5 and 6 effecting loss of water from hexanol *via* five- and six-membered cyclic transition states are shown in Figure 3. The results are presented in the form of phenomenological rate constants $\bar{k}(t)$. We base our discussion on ex-

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(25) The rate of formation of $C_3H_7^-$ at times $<2 \times 10^{-11}$ sec is probably enhanced by interaction with the external electric field. Reaction at times $>2 \times 10^{-11}$ sec is unaffected by external fields. For a discussion see H. D. Beckey, *Z. Naturforsch. A*, 19, 71 (1964).

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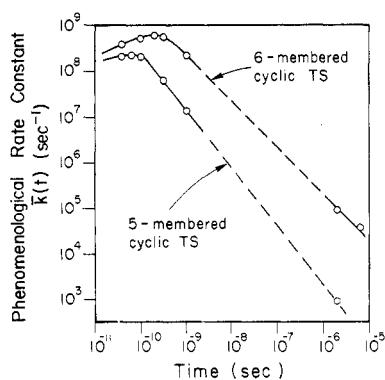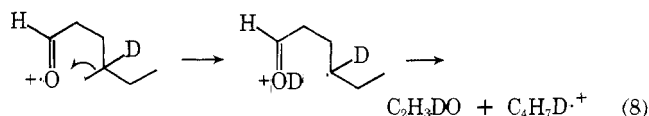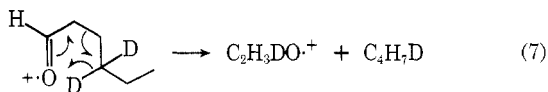(30) P. J. Derrick, A. M. Falick, and A. L. Burlingame, *J. Amer. Chem. Soc.*, 95, 437 (1973).

Figure 3. Phenomenological rate constants $\bar{k}(t)$ as a function of time for the reactions effecting loss of water from the hexanol radical cation *via* five-membered and *via* six-membered cyclic transition states.

Figure 4. The rates of formation of $C_2H_3DO\cdot^+$ and $C_4H_7D\cdot^+$ from the hexanal radical cation $C_6H_{10}D_2O\cdot^+$ as a function of time.

pression 4 from the statistical theory of unimolecular reactions. It can be assumed[30] that the kinetic data reflect the kinetics of the deuterium transfer. At the longest times (10^{-6} sec) the process *via* the six-membered transition state is predominant. As time decreases, the rate of the process *via* the five-membered transition state increases *relative* to that of the process *via* the six-membered. It follows[30] according to our previous argument (*vide supra*) that the six-membered transition state poses a lower energy barrier than the five-membered state. This is consistent with the prevalence of six-membered transition states throughout chemistry, both in the liquid and in the gas phase. The success of the process *via* the five-membered transition state at short times implies a higher density of states. This could be rationalized on the basis that formation of the six membered restricts four internal rotations, whereas formation of the five membered restricts only three. Alternatively, we could say that the five-membered transition state is the more "disordered," since one less carbon atom is confined within the ring.

FIK results for the two distinct reactions of aldehyde molecular ions involving γ-hydrogen transfer and β cleavage[31-33] were unexpected and intriguing. Figure 4 shows the results presented[31] as rates of reaction for hexanal-*4,4-d₂*. At times of a few $\times$ 10^{-11} sec the rate of formation of $C_2H_3DO\cdot^+$ exceeds the rate of formation of $C_4H_7D\cdot^+$ by almost an order of magnitude. At times of the order of 10^{-10} sec, however, the formation of $C_4H_7D\cdot^+$ is the faster reaction. The trend for the formation of $C_4H_7D\cdot^+$ to be faster at longer times is supported by measurements of metastable transitions (corresponding to reaction at 10^{-6} sec). The transition $C_6H_{10}D_2O^+ \rightarrow C_4H_7D\cdot^+ + C_2H_3DO$ is *at least* two orders of magni-

tude more intense than $C_6H_{10}D_2O^+ \rightarrow C_2H_3DO\cdot^+ + C_4H_7D$ (which cannot be detected at all). We hypothesize that the results can be explained on the basis of mechanisms 7 and 8. The formation of $C_2H_3DO\cdot^+$ *at times of the order of 10^{-11} sec* would be a concerted process, whereas the formation of $C_4H_7D\cdot^+$ *at times of the order of 10^{-10} sec and longer* would be a stepwise process involving an intermediate.

A theoretical treatment[3c] does suggest that the transition state in a stepwise process (such as in eq 8) has a lower energy than that in a concerted process (such as in eq 7). This would explain the predominant formation of $C_4H_7D\cdot^+$ at long times. According to our previous arguments, the dominant formation of $C_2H_3DO\cdot^+$ at short times implies a higher density of states in the transition state. This could be achieved by treating the restricted internal rotations as low frequency torsional vibrations in the concerted case, but as higher frequency out-of-phase ring vibrations in the stepwise process. That is to say, the concerted transition state is the "looser," because of the rupturing β bond. Assuming our explanations to be valid, the answer to the persistent and contentious question of whether γ-hydrogen transfers and β cleavages are stepwise or concerted would be "it depends on the time frame considered" —which is intuitively reasonable.

Hydrogen–Deuterium Rearrangements

It is a well-established fact that an isotopic label, for example deuterium, introduced into a molecule at a specific position may not remain in that position upon ionization.[2] Such apparently random rearrangements could indicate, as was pointed out by Stevenson and Wagner[34] over 20 years ago, that the species formed by gas-phase ionization are so highly energized that the fundamental concept of directed valence is no longer reliable. The success during the past decade in rationalizing the behavior of gaseous ions in conventional chemical terms[2] is good evidence that this is not the case, at least at low energies. However, to establish irrefutably the essentially conventional chemical nature of gas-phase ionic processes demands that isotopic rearrangements be explicable as isomerization in the usual chemical sense. This had proven to be difficult using the conventional EI techniques.[2] We feel we have been able to ad-

$$\text{(scheme)} \longrightarrow C_2H_3DO\cdot^+ + C_4H_7D \qquad (7)$$

$$\text{(scheme)} \longrightarrow \text{(scheme)} \longrightarrow$$

$$C_2H_3DO + C_4H_7D\cdot^+ \qquad (8)$$

(31) P. J. Derrick, A. M. Falick, and A. L. Burlingame, *J. Amer. Chem. Soc.*, 96, 615 (1974).

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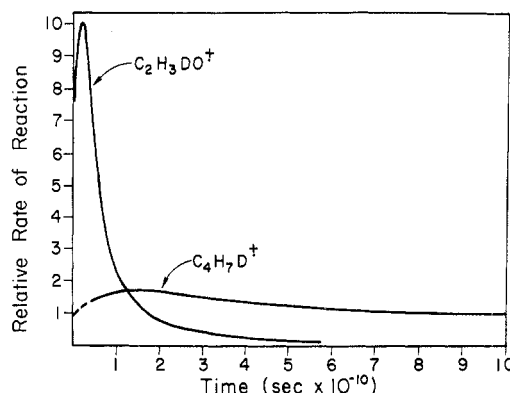
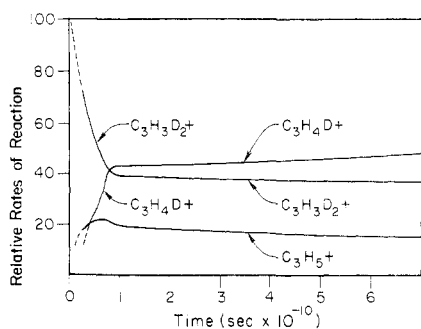(34) D. P. Stevenson and C. D. Wagner, *J. Chem. Phys.*, 19, 11 (1951).

Figure 5. Relative rates of formation of $C_3H_3D_2^+$, $C_3H_4D^+$, and $C_3H_5^+$ as a function of time following FI of 2-methylpropene-*1,1*-*d₂*.
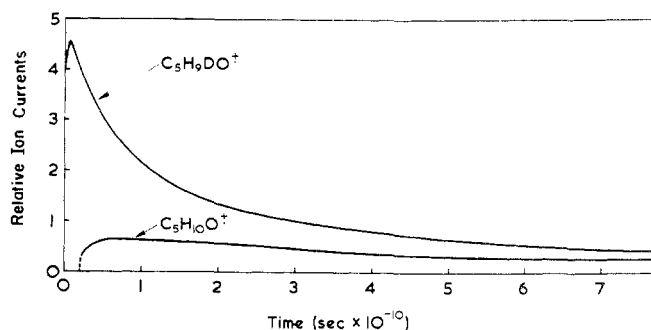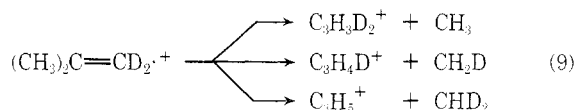

Figure 6. The formation of $C_4H_9DO\cdot^+$ and $C_5H_{10}O\cdot^+$ as a function of time following FI of 7-methyl-4-octanone-*7-d₁*.

vance the problem using the FIK technique.

Consider 2-methylpropene. The major reaction at times of 10^{-11} to 10^{-5} sec following ionization is loss of a methyl radical.[35] FI of the deuterated species, 2-methylpropene-*1,1-d₂* [$(CH_3)_2C{=}CD_2$], induces loss not only of $CH_3\cdot$ but also $CH_2D\cdot$ and $CHD_2\cdot$ (eq 9).

$$(CH_3)_2C{=}CD_2\cdot^+ \longrightarrow \begin{cases} C_3H_3D_2^+ & + \ CH_3 \\ C_3H_4D^+ & + \ CH_2D \\ C_3H_5^+ & + \ CHD_2 \end{cases} \qquad (9)$$

Evidently there has been rearrangement prior to fragmentation. It is such rearrangement which has been referred to as hydrogen–deuterium (H–D) "randomization." FIK results[35] for the various processes are shown in Figure 5. *Relative* rates of reaction are plotted as functions of time. We suggest that the dependence on time of the relative rates of reaction reflects the progress of rearrangement within the reactant species prior to fragmentation. Careful consideration[35] of the curves (Figure 5) leads to the conclusion that rearrangement and fragmentation proceed as in Scheme I. The relative rates over the time interval from 1×10^{-10} sec to 7×10^{-10} sec are steadily approaching the values predicted assuming a statistical mixture of the four 2-methylpropene isomers in Scheme I. The metastable intensities for the three reactions (at 10^{-6} sec) are in the statistical ratio. The maximum in the $C_3H_5^+$ curve at 7×10^{-11} sec can be associated with a transient high proportion of the isomer b in the isomeric mixture.[35] The rearrangement in 2-methylpropene is thus attributed to rapid 1,3 allylic hydrogen shifts.

FIK studies of partially deuterated but-1-ene[36] and cyclohexene[37] yield similar results. The frag-

Scheme I: 2-Methylpropene-1,1-*d₂*
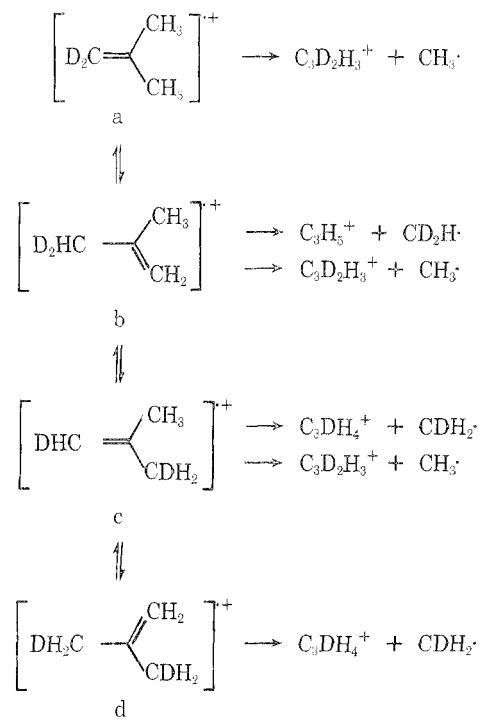
mentation reactions monitored were the loss of a methyl radical with but-1-ene and the retro-Diels–Alder elimination of ethylene with cyclohexene. We find the same dependence on time for the rates of formation of different isotopic isomers. The H and D loss as methyl radical or ethylene is random at long times (10^{-6} sec), but the fragmentations become increasingly specific as shorter times (10^{-11} sec) are considered. The H–D rearrangement processes are again identified as very rapid 1,3 allylic hydrogen (deuterium) shifts, although in the but-1-ene case other reactions are involved as well.[36] These 1,3 allylic hydrogen shifts may be further examples of symmetry-forbidden 1,3 sigmatropic reactions.[38]

Consider now aliphatic ketones. With straight-chain ketones there is a small amount of apparently random H–D rearrangement prior to fragmentation at times of the order of microseconds following ionization;[39] it is unlikely that isotopic rearrangement occurs at shorter times.[39] H–D rearrangement in the α-branched and α-deuterio-labeled 3-methyl-2-heptanone-*1,1,1,3-d₄* shows the same characteristics as that in the straight-chain ketones.[40] H–D rearrangement in the γ-branched and γ-deuterio-labeled 7-methyl-4-octanone-*7-d₁*, however, differs drastically.[40] Consider the FIK results in Figure 6. The ion currents are related to rates of reaction by expression 2; the ratio of the ion currents at any particular time t represents the relative rates of reaction at that time. The species $C_5H_9DO\cdot^+$ is the expected product of the McLafferty rearrangement (γ-deuterium transfer and β cleavage). H–D rearrangement so as to replace D by H at the γ position prior to the McLafferty rearrangement produces $C_5H_{10}\cdot^-$. The

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(36) P. J. Derrick, A. M. Falick, and A. L. Burlingame, *Advan. Mass Spectrom.*, **6**, 877 (1974).

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

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(39) P. J. Derrick, A. M. Falick, S. Lewis, and A. L. Burlingame, *Org. Mass Spectrom.*, **7**, 887 (1973).
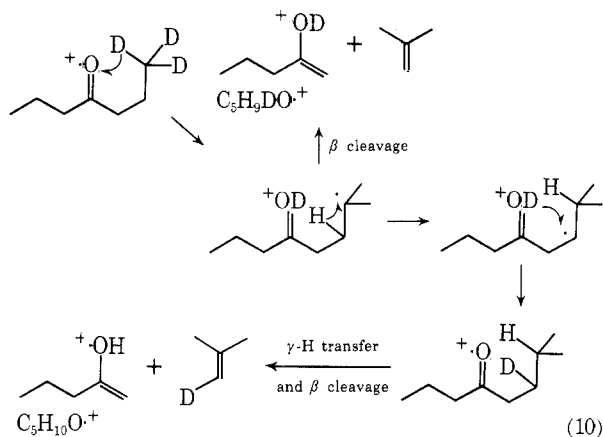
(40) P. J. Derrick, A. M. Falick, A. L. Burlingame, and C. Djerassi, *J. Amer. Chem. Soc.*, **96**, 1054 (1974).

apparently random H–D rearrangement is thus able to compete successfully with the McLafferty rearrangement, even at times less than 10^{-10} sec.

To explain these kinetic results we propose the following mechanism[41]

We are concerned primarily with reaction at times of 10^{-10} sec and longer, at which times we consider the McLafferty rearrangement to be stepwise (*cf.* hexanal). The crucial question is: does the species formed by the initial γ-D transfer undergo hydrogen shifts in the hydrocarbon chain or does it undergo β cleavage? We argue that the tertiary radical formed by γ transfer in a γ-branched molecule is significantly more stable than the secondary radical formed with a straight-chain or α-branched molecule, and that the increased stability will favor hydrogen shifts over β cleavage.[40] Thus branching at the γ position enables H–D rearrangement to compete more effectively with McLafferty rearrangement. Support for the proposed mechanism (eq 10) can be derived from the relative rates of McLafferty rearrangement in straight-chain and γ-branched ketones.[40]

The point we wish to make is that the apparently random H–D rearrangements in aliphatic alkenes and ketones are explicable in terms of perfectly conventional chemical reactions. We suggest that this is generally true for aliphatic species.[42] The only probable exceptions are alkane ions.[21] Hydrogen and deuterium atoms in aliphatic ions containing unsaturation or functional groups arrive at a degree of isotopic randomization by a series of highly specific hydrogen (deuterium) shifts.

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(42) See D. J. McAdoo, F. W. McLafferty, and T. E. Parks, *J. Amer. Chem. Soc.*, 94, 1601 (1972).

Long-Range Carbon–Proton and Carbon–Carbon Spin–Spin Coupling Constants

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Received April 10, 1974

During the 1960's a profusion of experimental proton nmr data, in conjuction with excellent theoretical work, allowed very satisfactory correlation of molecular structure with proton–proton spin–spin coupling constants.[1] This correlation has given the organic chemist a powerful tool for structure elucidation of even very complex molecules. Proton nmr work was so fruitful because of three inherent features: (1) the ubiquitousness of the proton in organic molecules, giving the nmr spectroscopist an almost unlimited number of systems to explore; (2) the high natural abundance of the ^{1}H isotope (99.98%), whose spin of $\frac{1}{2}$ gives sharp signals, allowing precise measurements of high-resolution spectra; (3) the high sensitivity of the ^{1}H nucleus, and hence the large nmr signals.

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Carbon–Proton Couplings. It would seem desirable to extend structural correlations to carbon–proton couplings, since carbon exists in all organic compounds, by definition. However, the common isotope of carbon—^{12}C, whose nuclear spin is 0—is nmr inactive, and carbon–proton couplings are not a significant feature in routine proton nmr spectra. Actually, the nmr inactivity of carbon-12 has been a blessing during the extensive proton–proton investigations of the past 15 years, because it removed the complication of carbon–proton couplings. Now that our understanding of proton–proton couplings is fairly complete, however, the attractiveness of additional nmr methods involving carbon increases. The isotope of carbon that *is* nmr active (^{13}C, with a nuclear spin of $\frac{1}{2}$) exists in nature to the extent of 1.1%. Hence, if one chooses a system wherein the main proton signals do not mask the much weaker signals arising from the carbon–proton couplings, one may obtain accurate measurements for these couplings. In practice, only large carbon–proton splittings may be observed,

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