1.3442 (lit.[28] bp 81.6°, n^{20}D 1.34423). Likewise, pyruvic acid was purified just before use by distillation at reduced pressure, bp 71.2–72.2° (22 mm), n^{20}D 1.4272 (lit.[29] bp 75–80° (25 mm), n^{20}D 1.4280).

Samples tubes (4 mm i.d. Pyrex) were charged with 0.0109 ± 0.0003 g of olefin (7.26 × 10^{-5} mol), 0.0026 ± 0.0001 g of pyruvic acid (3.0 × 10^{-5} mol), and 0.0355 ± 0.005 g of acetonitrile. Olefin concentration at the reaction temperature was 1.10 ± 0.03 M. After the tubes were sealed to a length of approximately 5 cm, they were placed in the oil bath (time = 0).

At measured intervals, the reactions were quenched by plunging the tubes in ice-water. After 50 μl of CCl_4 was added to each tube to effect solution, the contents were analyzed by gas chromatography (column C).

Analysis of Errors. The gas chromatographic response (thermal conductivity) to the three isomeric olefins was considered uniform and was linear with the sample sizes used. The peak areas, determined by planimetry, were reproducible to less than 1% for all peaks except the minor ones, which were subject to significantly

greater error. The precision of peak area measurements of duplicate injections of the same sample was less than 2% for major peaks.

Each of the olefins (1–3) was collected individually from the gas chromatograph and analyzed for decomposition during chromatographic analysis. The nuclear magnetic resonance spectra and gas chromatograms of the collected samples were identical with those of the original compounds. Likewise, the chromatogram of a known mixture of the olefins in pyruvic acid–acetonitrile, dissolved in carbon tetrachloride, prepared for calibration purposes, indicated that no detectable isomerization was taking place in the gas chromatograph.

To estimate the error in the values of the slopes generated by the least-squares analyses (and thus the error in the observed rate constants), the standard deviation of the slope, σ, was estimated by

$$\sigma = \left[\frac{n}{n \sum X_i^2 - (\sum X_i)^2} \frac{\sum d_i^2}{n-2} \right]^{1/2}$$

with n, the number of experimental points; X_i, the ith X (time) value; and d_i, the difference for the ith point between the calculated value for log [olefin] and the observed value. The "Student t distribution" was used to obtain the 95% confidence interval.

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Progressive Specific Hydrogen Rearrangements Quenched by Molecular Ion Fragmentation in 2-Methylpropene. Mass Spectral Serendipity[1]

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Contribution from the Space Sciences Laboratory, University of California, Berkeley, California 94720. Received September 7, 1972

Abstract: The loss of a methyl radical from 2-methylpropene, 2-methylpropene-*1,1-d₂*, and 2-methyl-*d₃*-propene-*3,3,3-d₃* has been studied at times from 10^{-11} to 10^{-6} sec following field ionization (FI). Considerable rearrangement of the H and D in the deuterated species occurs prior to fragmentation even at times as short as a few × 10^{-11} sec. The rearrangement leads to almost complete H–D randomization prior to fragmentation at 7 × 10^{-10} sec. The observed H–D randomization may be rationalized in terms of successive isomerizations *via* 1,3 allylic hydrogen shifts. The electron impact (EI) mass spectra of 2-methylpropene, 2-methylpropene-*1,1-d₂*, and 2-methyl-*d₃*-propene-*3,3,3-d₃* have been measured at high and low ionizing energies and are discussed in relation to the FI results.

It is recognized that the unimolecular reaction systems set up by gas-phase ionization of alkenes are typically extremely complex.[3] The mass spectra of isotopically labeled species show that extensive molecular rearrangement leading to randomization of the labels tends to occur either prior to or as an integral part of fragmentation.[4–7] The nature of the rearrange-

ment processes remains, however, largely a matter of conjecture, even for the smallest molecules such as propenes and butenes. It has been proposed that the processes leading to hydrogen randomization in the propene ion involve only 1,3 shifts.[6b,c] Other workers have suggested that both 1,2 and 1,3 shifts are operative.[6d] Yet again it has been suggested that randomization in propene, butene, and pentene radical-ions is predominantly due to 1,2-hydrogen shifts.[6e] 1,3-Allylic hydrogen shifts have been envisaged to occur in the $\Delta^{4(8)}$-menthene[7] and methylcyclohexene[8] radical-ions. McLafferty, *et al.*,[9] have proposed that closely analogous 1,3-hydrogen shifts occur in the enolic $C_3H_6O \cdot^+$ ion. Conversely, however, it has been suggested[10] that whereas 1,2-, 1,4-, and 1,5-hydrogen shifts are in general facile unimolecular reactions of radical-cations, 1,3-

(1) The work was performed in collaboration with Dr. A. M. Falick who is also responsible for the computation of lifetimes. See J.-P. Pfeifer, A. M. Falick, and A. L. Burlingame, *Int. J. Mass Spectrom. Ion Phys.*, **11**, 345 (1973).

(2) (a) Present address: Department of Chemistry, University College, University of London, London WC1H 0AJ, England; (b) John Simon Guggenheim Memorial Fellow, 1970–1972.

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

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(8) T. H. Kinstle and R. E. Stark, *J. Org. Chem.*, **32**, 1318 (1967).

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(10) M. T. Bowers, D. H. Aue, and D. D. Elleman, *J. Amer. Chem. Soc.*, **94**, 4255 (1972).
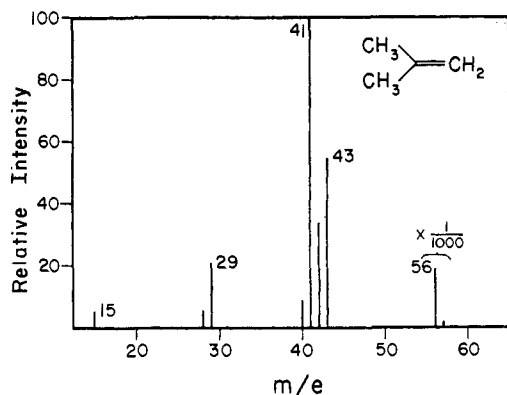
Figure 1. The "normal" FI mass spectrum of 2-methylpropene.

hydrogen shifts are not.[11,12] The earlier workers tended to neglect the possibility of carbon skeletal rearrangements. More recent work,[13-15] however, supports an early suggestion[5] that at least some alkene radical-ions can undergo skeletal rearrangement. The 1-butene radical-ion, for example, rearranges to the 2-methylpropene carbon skeleton structure even at very low energies[13,14] (photoionization with the argon resonance lines 11.6 and 11.8 eV). Carbon skeletal rearrangements of alkene radical-ions are not at all understood. Taking an overall view, the present understanding of the unimolecular gas-phase rearrangement and fragmentation of alkene radical-ions could justifiably be described as confused. It has become apparent that insight into the nature of processes occurring at rates too rapid to be directly observed by electron impact (EI) mass spectrometry may be gained by proper application of the field ionization kinetics (FIK) technique.[16,17] An earlier FIK study[18] provided considerable insight into the nature of the rearrangements and fragmentations of the cyclohexene radical-cation. Observed hydrogen randomization could be explained in terms of rapid 1,3 allylic hydrogen shifts around an intact cyclohexene ring. We now report FIK measurements on 2-methylpropene, 2-methylpropene-$1,1$-d_2 (1), and 2-methyl-d_3-propene-$3,3,3$-d_3

Figure 2. Measured curves of ion currents I_f as a function of blade potential for m/e 41 $(M - CH_3)^+$, m/e 40 $(M - CH_4) \cdot {}^+$, and m/e 42 $([M + 1] - CH_3)^+$ following FI of 2-methylpropene. I_M is the ion current of the molecular ion M^+ in the "normal" FI mass spectrum. Experimental data points are omitted due to their large number and low degree of scatter. The times quoted refer to the formation of m/e 41 $(M - CH_3)^+$.

(2). There is good evidence[14,19] that the 2-methylpropene radical-ion does not undergo skeletal rearrangement at low energies, so that any observed hydrogen randomization can be discussed with some confidence in terms of hydrogen shifts of some kind or another.

Experimental Section

The FIK measurements were made on a modified Du Pont (C.E.C.) 21-110B double focusing mass spectrometer.[20] The standard Du Pont combination FI/EI combination ion source incorporating a blade emitter was employed. The electron collimating magnet was removed to avoid mass discrimination. Source temperature was maintained at 200° during all of the reported experiments.

The theory[20-26] behind the field ionization kinetic measurements described here and a detailed description of the method employed[20] in obtaining our results have been presented previously, so that only a few brief comments need be given here. The magnetic analyzer was focused on the fragment ion of interest and the blade potential V_B was scanned from approximately 8 to 10 kV in 10-V steps. The resulting quasicontinuous curves could be converted to curves of fragment ion current (or rate of fragment ion formation) vs. time.[1,20] The shapes of these curves are dependent on source temperature[27] and conditions of the blade surface.[21,28]

EI mass spectra were measured on a G.E.C.-A.E.I. MS 902 mass

(11) Direct quantitative data on hydrogen shifts in carbonium ions in the liquid phase have recently been provided (M. Saunders and J. J. Stofko, J. Amer. Chem. Soc., 95, 252 (1973)). Rearrangement of the 2,4-dimethyl-2-pentyl cation does not proceed via successive 1,2-hydrogen shifts. Rather, 1,3-hydrogen shift occurs. The much studied propyl cation rearranges by 1,3 instead of by successive 1,2-hydrogen shifts. For a review, see J. L. Fry and G. J. Karabatsos in "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, pp 521–572.

(12) 1,3-Hydrogen shifts are well known in free-radical chemistry. In contrast, the efforts to securely establish the occurrence of a 1,2-hydrogen shift within a free-radical have as yet been unsuccessful. For a review see W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966.

(13) G. G. Meisels, J. Y. Park, and B. G. Giessner, J. Amer. Chem. Soc., 91, 1555 (1969).

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(16) We define data as to the kinetics of unimolecular gas-phase reactions at times from 10^{-11} sec (or in some cases 10^{-12} sec) to 10^{-5} sec following field ionization as "field ionization kinetics." See P. J. Derrick, A. M. Falick, and A. L. Burlingame, 20th Annual Conference on Mass Spectrometry and Allied Topics, Dallas, Texas, June 1972, Paper No. H4.

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

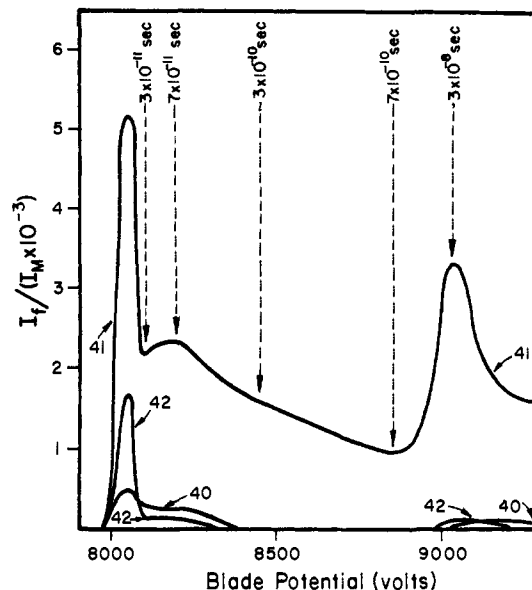(18) P. J. Derrick, A. M. Falick, and A. L. Burlingame, J. Amer. Chem. Soc., 94, 6794 (1972).

(19) S. G. Lias and P. Ausloos, J. Res. Nat. Bur. Stand., Sect. A, 75, 59 (1971).

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(23) H. D. Beckey and H. Knoppel, Z. Naturforsch. A, 21, 1920 (1966).

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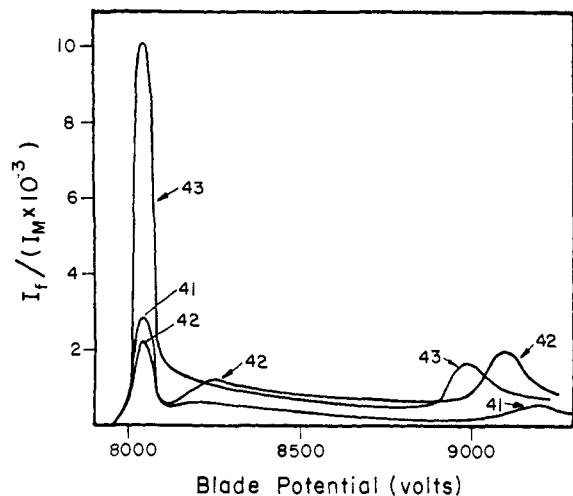(28) P. J. Derrick and A. J. B. Robertson, Int. J. Mass. Spectrom. Ion Phys., 10, 315 (1973).

Figure 3. Measured curves of ion currents I_f as a function of blade potential for m/e 41 (M $-$ CD$_2$H)$^+$, m/e 42 (M $-$ CDH$_2$)$^+$, and m/e 43 (M $-$ CH$_3$)$^+$ following FI of 2-methylpropene-$1,1$-d_2 (1). I_M is the ion current of the molecular ion M$^+$ in the "normal" FI mass spectrum. Experimental data points are omitted due to their large number and low degree of scatter.

Figure 4. Measured curves of ion currents I_f as a function of blade potential for m/e 44 (M $-$ CD$_3$)$^+$, m/e 45 (M $-$ CD$_2$H)$^+$, and m/e 46 (M $-$ CDH$_2$)$^+$ following FI of 2-methyl-d_3-propene-$3,3,3$-d_3 (2). I_M is the ion current of the molecular ion M$^+$ in the "normal" FI mass spectrum. Experimental data points are omitted due to their large number and low degree of scatter.

spectrometer on-line to an XDS Sigma 7 computer.[29] Source temperature was maintained at 50°.

Both deuterated propenes 1 and 2 supplied by Merck, Sharp and Dohme Ltd., Montreal, were found by mass spectrometry to have isotopic purities of 98 atom %.

Results

The "normal" FI mass spectrum of 2-methylpropene is given in Figure 1. The "normal" FI mass spectrum obtained with a double focusing analyzer displays only the ionic products of reactions occurring on the blade surface or in the immediate vicinity of the blade.[20] The "normal" spectrum is obtained when the blade voltage is approximately equal to the normal accelerating voltage.[30]

Figure 2 gives the ion currents for the fragment ions m/e 40, 41, and 42 as a function of blade potential. The ion currents at blade voltages greater than about 8100 V are due entirely to gas-phase unimolecular decompositions.[20] The ion currents at $V_B < 8100$ V represent ions formed on and very close to the blade surface. The maxima in the ion currents in Figure 3 at $V_B > 9000$ V represent fragmentation occurring between the focus electrodes.[12,20] The ions m/e 40, 41, and 42 are the only fragments formed between the blade and the cathode outside of the high field (i.e., at times $> \sim 3 \times 10^{-11}$ sec) following FI of 2-methylpropene.

Following field ionization of the deuterated species 2-methylpropene-$1,1$-d_2 (1), three fragments m/e 41, 42, and 43 are formed at significant intensities between the blade and the cathode outside of the high-field region. Similarly 2-methyl-d_3-propene-$3,3,3$-d_3 (2) yields three fragments m/e 44, 45, and 46. The ion currents I_f of these fragments as functions of blade potential V_B are shown in Figures 3 and 4. The maxima at around 9000 V in both figures are as before due to fragmenta-

tion between the focus electrodes. The curves of ion current I_f against blade potential V_B between $V_B = $ 8100 V and about $V_B = 8900$ V have been transformed to curves of ion current $I_f(t)$ against molecular ion lifetime in Figures 5 and 6. The ion current I_f at $V_B < $ 8100 V is not considered since these ions may arise from surface or high-field processes. The ratios of the currents $I_f(t)$ at any particular time within either Figure 5 or 6 are equal to a good approximation to the ratios of the rates of formation of the fragment ions.[20]

The electron impact (EI) mass spectra of 2-methylpropene, 1, and 2 at low and high electron energies are presented in Figure 7.

The relative intensities of the fragments m/e 41, 42, and 43 from 1 and of m/e 44, 45, and 46 from 2 at different times after FI and the relative intensities of these ions in the low and high energy EI spectra are displayed in Table I. The FI intensities at times less than and including 3×10^{-8} sec are based on Figures 3–6. The intensities at 10^{-6} sec following FI are based on metastable transitions in the field-free region between the ion source and the electric sector measured by the now well-established "metastable defocusing technique" of lowering the electric sector potential.[31]

Discussion

Field Ionization Kinetics. Our interests in this FIK investigation of 2-methylpropene concern unimolecular reactions taking place in the gas phase beyond the influence of the very high external electric fields in the immediate vicinity of the blade.[32] Conclusions reached in the FI study can then be *tentatively* extrapolated to low energy (10–12 eV), and possibly high energy (70 eV),

(29) A. L. Burlingame in "Recent Developments in Mass Spectroscopy," K. Ogata and T. Hayakawa, Ed., University Park Press, Baltimore, Md., 1970, p 104.

(30) The blade voltage differs from the normal accelerating voltage by a small correcting term. See A. J. B. Robertson and B. W. Viney, *J. Chem. Soc. A*, 1843 (1966).
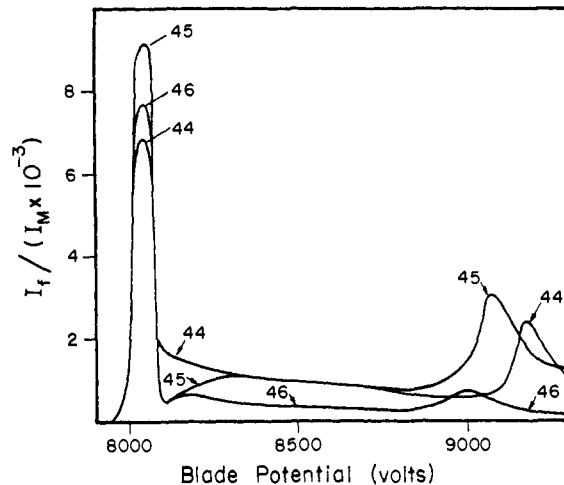
(31) (a) M. Barber and R. M. Elliott, 12th Annual Conference on Mass Spectrometry and Allied Topics, Montreal, June 1964, Paper No. 22; (b) L. P. Hills and J. H. Futrell, *Org. Mass Spectrom.*, 5, 1019 (1971).

(32) Generally speaking "normal" FI mass spectra are not reliable bases for mechanistic inference for *unimolecular gas-phase* reactions. The reactions contributing to the "normal" FI mass spectrum may be catalyzed by the emitter surface, often occur in a liquid phase at the surface, and generally are influenced by the very high field in the vicinity of the emitter. See, for example, P. Brown and C. Fenselau, *Org. Mass Spectrom.*, 7, 305 (1973); E. M. Chait and F. G. Kitson, *ibid.*, 3, 533 (1970).
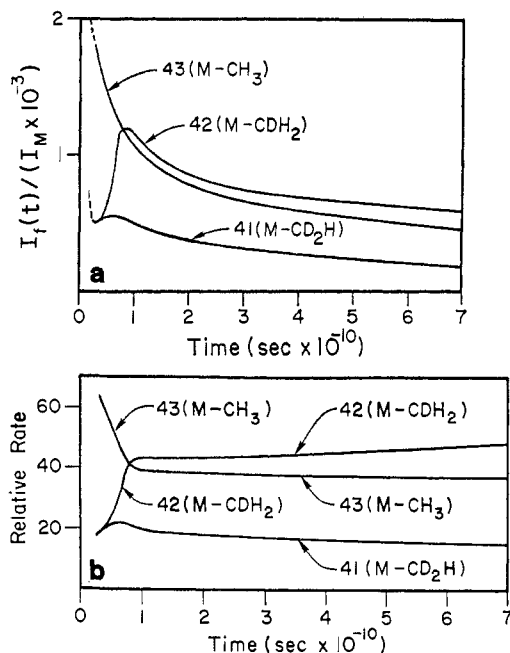
Figure 5. (a) Ion currents $I_f(t)$ due to m/e 41 (M − CD_2H)$^+$, m/e 42 (M − CDH_2)$^+$, and m/e 43 (M − CH_3)$^+$ from 2-methylpropene-$1,1$-d_2 (1) as a function of molecular ion lifetime following FI. The lifetimes are calculated from the blade potentials in Figure 3. I_M is the ion current of the molecular ion M$^+$ in the "normal" FI mass spectrum. (b) Relative rates of formation of m/e 41 (M − CD_2H)$^+$, m/e 42 (M − CDH_2)$^+$, and m/e 43 (M − CH_3)$^+$ from 2-methylpropene-$1,1$-d_2 (1) as a function of molecular ion lifetime.
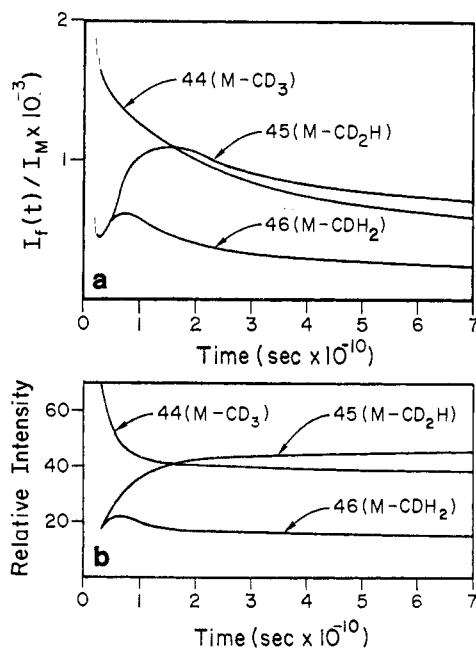
Figure 6. (a) Ion currents $I_f(t)$ due to m/e 44 (M − CD_3)$^+$, m/e 45 (M − CD_2H)$^+$, and m/e 46 (M − CDH_2)$^+$ from 2-methyl-d_3-propene-$3,3,3$-d_3 (2) as a function of molecular ion lifetime following FI. The lifetimes are calculated from the blade potentials in Figure 4. I_M is the ion current of the molecular ion M$^+$ in the "normal" FI mass spectrum. (b) Relative rates of formation of m/e 44 (M − CD_3)$^+$, m/e 45 (M − CD_2H)$^+$, and m/e 46 (M − CDH_2)$^+$ from 2-methyl-d_3-propene-$3,3,3$-d_3 (2) as a function of molecular ion lifetime.

EI reaction systems. Following FI the parent ions move rapidly away from the blade surface in the high-potential gradient, and arrive at regions where the external
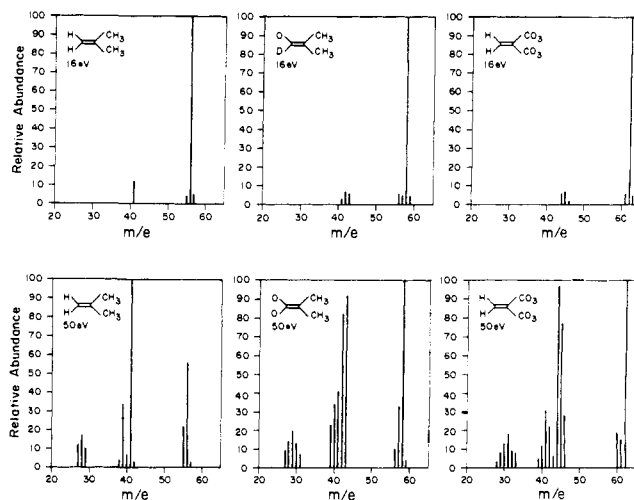

Figure 7. EI mass spectra of 2-methylpropene, 2-methylpropene-$1,1$-d_2 (1), and 2-methyl d_3-propene-$3,3,3$-d_3 (2) at 50 eV and nominally 16 eV ionizing electron energies. Ions with intensities of <1% relative to the most intense ion in a spectrum have been omitted.

electric fields are insignificant compared to the internal electric fields of the molecule within 2 or 3 × 10^{-11} sec.[20,21] We are interested in fragment ions formed at times > 3 × 10^{-11} sec (Figures 2, 5, and 6). The formation of the fragment m/e 41 from 2-methylpropene at times >3 × 10^{-11} sec following FI is interpreted as the elimination of a methyl radical from the molecular ion. The less important (for the purposes of our discussion) fragments m/e 40 and 42 at times >3 × 10^{-11} sec are attributed to loss of methane from the molecular ion and loss of a methyl radical from the protonated species (M + 1)$^+$, respectively. Transitions 56$^+$ → 40$^+$ and 57$^+$ → 42$^+$ are observed at low intensities in the first field-free region. The formation of protonated molecular ions (M + 1)$^+$ in reactions at the surface is very common following FI.[33] Phenomenological rate constants $\bar{k}(t)$ have been calculated for the formation of m/e 41 (M − CH_3) from 2-methylpropene (see Figure 8) using the relationship[20,33]

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

In an earlier paper,[18] we referred to $\bar{k}(t)$ as an "average rate constant." We now prefer the term "phenomenological rate constant," since this emphasizes that $\bar{k}(t)$ is basically an experimental quantity and, further, emphasizes the close analogy with phenomenological rate constants of ion-molecule reactions. Accordingly we refer to the theoretical rate constant k describing the ideal situation in which all reactant molecules possess the same discrete amount of internal energy as a "microscopic rate constant." The quantities on the right-hand side of the relationship (eq 1) are as follows: $I_f(t)$ is the m/e 41 (M − CH_3) ion current at time t, $I_M(t)$ is the ion current of undecomposed molecular ions m/e 58 (M) at that time, and Δt is the time interval over which the fragment ions contributing to $I_f(t)$ are formed. The values of $I_f(t)$ at 10^{-11}–10^{-9} sec are taken from Figure 2. The value at 10^{-6} sec is the metastable intensity in the first field-free region. $I_M(t)$ is replaced by the molecular ion current I_M in the "normal" FI mass

(33) See H. D. Beckey, "Field Ionization Mass Spectrometry," Pergamon Press, New York, N. Y., 1971.

Table I. Measured Relative Intensities of Fragment Ions Formed by Loss of a Methyl Radical from 2-Methylpropene-$1,1$-d_2 (1) and 2-Methyl-d_3-propene-$3,3,3$-d_3 (2) at Various Times Following FI and Following EI. The Calculated Relative Intensities Assuming Complete Randomization of H–D Prior to Loss of Methyl Are Given for Comparison

	2-Methylpropene-$1,1$-d_2 (1)			2-Methyl-d_3-propene-$3,3,3$-d_3 (2)		
	—————m/e—————			—————m/e—————		
	41	42	43	46	45	44
	$(M - CD_2H)^+$	$(M - CDH_2)^+$	$(M - CH_3)^+$	$(M - CDH_2)^+$	$(M - CD_2H)^+$	$(M - CD_3)^+$
Calculated (complete H–D randomization)[a]	11	54	36	11	54	36
Field ionization						
3×10^{-11} sec	18	18	63	18	18	65
1×10^{-10} sec	18	43	39	20	36	44
7×10^{-10} sec	15	48	37	15	46	39
3×10^{-8} sec (at focus electrodes[b])	14	47	39	12	49	39
1×10^{-6} sec (metastables in first field-free region)	10	51	39	11	55	34
Electron impact						
50 eV[c]	19	38	43	14	38	48
Nominally 16 eV	13	49	38	12	50	38

[a] Statistical mixture of all possible 2-methylpropene isotopic isomers. [b] Small errors will be present in these figures due to contributions from fragments formed between the blade and the cathode (i.e., at times $\sim 10^{-9}$ sec). [c] With 2-methylpropene-$1,1$-d_2 (1), the measured intensity of m/e 41 probably contains a significant contribution from $C_3D_2H^+ (M - CH_3 - H_2)^+$.

spectrum. The estimation of Δt has been described.[1,12,20] A linear dependence of the phenomenological rate constants on time such as we find for the formation of m/e 41 (M — CH$_3$) has been found for many other unimolecular gas-phase reactions induced by field ionization.[12,24,33,34] As far as can be assessed, the linearity in Figure 8 extends from 10^{-10} to 10^{-6} sec. At times less than 1×10^{-10} sec, $\bar{k}(t)$ is approximately independent of time. The variation in the magnitude of the phenomenological rate constant $\bar{k}(t)$ from 10^7 to 10^3 sec^{-1} would suggest that a *distribution* of microscopic rate constants k is necessary for an adequate description of the reaction. A distribution of microscopic rate constants k might arise if different amounts of internal energy E were imparted to different molecules by the ionization process. More energetic ions react at higher rates and therefore at shorter times. As time progresses, so the reaction observed is that of progressively less energetic ions. Consequently the observed reaction rate and the phenomenological rate constant decline with time. The time independence of $\bar{k}(t)$ at the shortest times can be explained as follows. The explanation derives from Beckey and colleagues.[34c,d,35] Assuming the basic tenets of the quasi-equilibrium theory[36] to be valid and making certain reasonable assumptions[34c,d] as to the form of the distribution of microscopic rate constants k, it can be shown[34c,d] that the phenomenological rate constant $\bar{k}(t)$ will be approximately independent of time at times less than the reciprocal of the maximum microscopic rate constant k_{max} in the distribution of microscopic rate constants. This happens since at these times reaction can be described by just the one maximum microscopic rate constant k_{max}. According to this theory, the change in slope at about 1×10^{-10} sec in Figure 8

Figure 8. The logarithm of the phenomenological rate constant $\bar{k}(t)$ for the formation of m/e 41 $(M - CH_3)^+$ from 2-methylpropene as a function of the logarithm of the molecular ion lifetime following FI. Correction has been made for the increase in total emission on raising the blade potential.

must represent the reciprocal of k_{max}, so that k_{max} for the loss of a methyl radical from the 2-methylpropene molecular ion (outside of the very high field region) is about 5×10^9 sec^{-1} (a symmetry factor of 2 must be considered). This figure represents the maximum possible rate of reaction given the amount of excitation energy available from FI under the particular conditions employed. The reaction almost certainly proceeds more rapidly at higher energies (e.g., following 70 eV EI).

We attribute the fragments formed from the deuterated species at times from 3×10^{-11} to 10^{-9} sec to loss of methyl radicals from the molecular ions (and isotopic isomers thereof). Contributions from other fragmentation processes can be safely neglected. The fragments are thus identified as $(M - CD_2H)$ m/e 41, $(M - CDH_2)$ m/e 42, and $(M - CH_3)$ m/e 43 from 1 (Figures 4 and 6), and $(M - CD_3)$ m/e 44, $(M - CD_2H)$ m/e 45, and $(M - CDH_2)$ m/e 46 from 2 (Figures 4 and 6). The observation of three fragment ions with each of the deuterated species 1 and 2 corresponding to a single fragment $(M - CH_3)^+$ with the undeuterated species establishes that considerable rearrangement occurs

(34) (a) G. Tenschert and H. D. Beckey, *Ber. Bunsen. Phys. Chem.*, 72, 1039 (1968); (b) H. D. Beckey, *Z. Naturforsch. A*, 26, 1243 (1971); (c) G. Tenschert and H. D. Beckey, *Int. J. Mass Spectrom. Ion Phys.*, 7, 97 (1971); (d) K. Levsen and H. D. Beckey, *ibid.*, 7, 341 (1971); (e) *ibid.*, 9, 51 (1972); (f) *ibid.*, 9, 63 (1972); (g) P. J Derrick, A. M. Falick, and A. L. Burlingame, *J. Amer. Chem. Soc.*, 95, 437 (1973); (h) P. J. Derrick, A. M. Falick, S. Lewis, and A. L. Burlingame, *Org. Mass Spectrom.*, 7, 887 (1973).

(35) H. D. Beckey, private communication.

(36) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Nat. Acad. Sci. U. S.*, 38, 667 (1952).
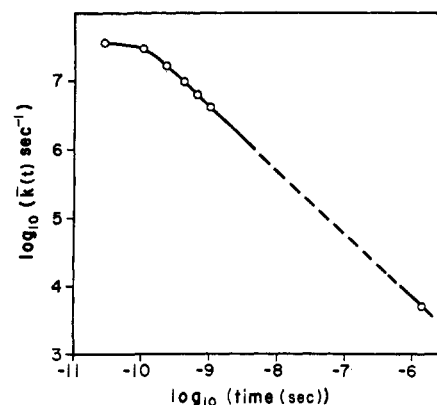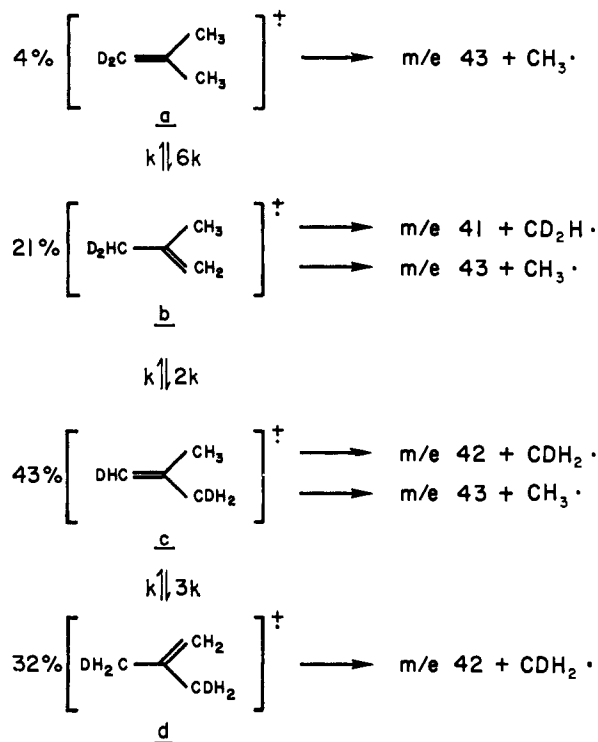
prior to fragmentation. It is evident (Figures 5 and 6 and Table I) that the relative intensities of these fragment ions from 1 and 2 are sensitive functions of time. We suggest that the progress of hydrogen rearrangement prior to fragmentation can be monitored by observation of the manner in which the different fragmentations depend upon time. Consideration of Figures 5 and 6 and Table I leads to the conclusion that rearrangement and fragmentation occur in the manner depicted in Schemes I and II. Rearrangement is pro-

Scheme I. 2-Methylpropene-$1,1$-d_2

4% $\left[D_2C \overset{CH_3}{\underset{CH_3}{\diagdown}} \right]^{+}$ a $\longrightarrow$ m/e 43 + CH$_3\cdot$

$k \Updownarrow 6k$

21% $\left[D_2HC \overset{CH_3}{\underset{CH_2}{\diagdown}} \right]^{+}$ b $\longrightarrow$ m/e 41 + CD$_2$H$\cdot$
                              $\longrightarrow$ m/e 43 + CH$_3\cdot$

$k \Updownarrow 2k$

43% $\left[DHC \overset{CH_3}{\underset{CDH_2}{\diagdown}} \right]^{+}$ c $\longrightarrow$ m/e 42 + CDH$_2\cdot$
                              $\longrightarrow$ m/e 43 + CH$_3\cdot$

$k \Updownarrow 3k$

32% $\left[DH_2C \overset{CH_2}{\underset{CDH_2}{\diagdown}} \right]^{+}$ d $\longrightarrow$ m/e 42 + CDH$_2\cdot$

Scheme II. 2-Methyl-d_3-propene-$3,3,3$-d_3 (2)

4% $\left[H_2C \overset{CD_3}{\underset{CD_3}{\diagdown}} \right]^{+}$ a $\longrightarrow$ m/e 44 + CD$_3\cdot$

$k \Updownarrow 6k$

21% $\left[DH_2C \overset{CD_3}{\underset{CD_2}{\diagdown}} \right]^{+}$ b $\longrightarrow$ m/e 44 + CD$_3\cdot$
                              $\longrightarrow$ m/e 46 + CDH$_2\cdot$

$k \Updownarrow 2k$

43% $\left[DHC \overset{CD_3}{\underset{CD_2H}{\diagdown}} \right]^{+}$ c $\longrightarrow$ m/e 44 + CD$_3\cdot$
                              $\longrightarrow$ m/e 45 + CD$_2$H$\cdot$

$4k \Updownarrow 3k$

32% $\left[D_2HC \overset{CD_3}{\underset{CD_2H}{\diagdown}} \right]^{+}$ d $\longrightarrow$ m/e 45 + CD$_2$H$\cdot$
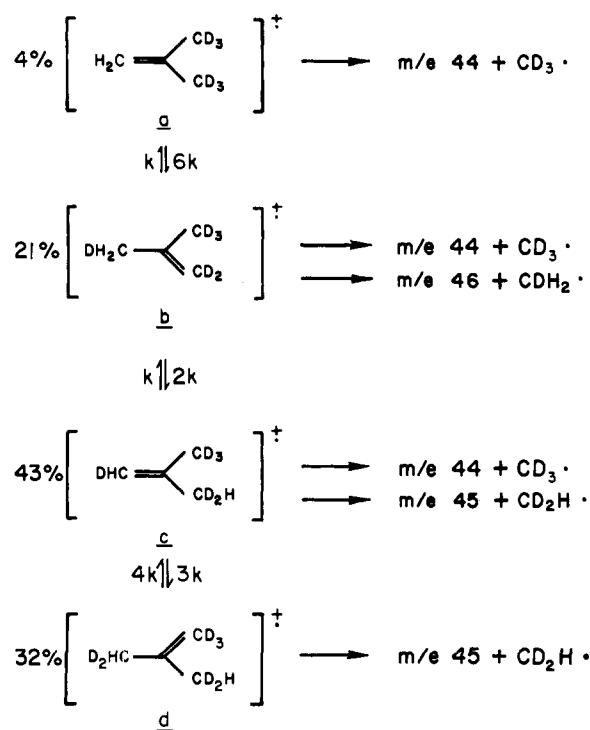
posed to occur via 1,3-hydrogen shifts. The rate constants for the various isomeric interconversions are given in Schemes I and II in terms of the rate constant for a 1,3 hydrogen or deuterium shift. We consider the rates of hydrogen and deuterium transfer to be equal since the results suggest that any isotope effect is small.[37] The relative amounts of the different isomers in the statistical mixtures of the isomers are given as percentages in Schemes I and II. The mechanistic Schemes I and II satisfactorily explain the kinetic results. The discussion is similar with both 1 and 2, so we shall consider only 1. The relative intensity of m/e 43 (M − CH$_3$) declines with increasing time from a level considerably in excess of the statistical value at 3 × 10^{-11} sec to approximately the statistical value at 1 × 10^{-6} sec (Figure 5b and Table I). By statistical value we mean the relative intensity expected given a statistical mixture of all possible isotopic isomers a, b, c, and d and an absence of isotope effects. We define such a statistical mixture of all possible isotopic isomers of the structural species as H–D randomization. We attribute the declining intensity of m/e 43 (M − CH$_3$) with time to the progressive rearrangement of the molecular ion a to the isomers b, c, and d. Whereas all fragmentation of a gives m/e 43 (M − CH$_3$), only half the fragmentation of b and c leads to m/e 43 (M − CH$_3$). The fragmentation of d does not give m/e 43 (M − CH$_3$) at all. That the relative intensity of m/e 43 (M − CH$_3$) at the shortest accessible time (3 × 10^{-11} sec) is 63%, rather than 100% as would be the case if only the molecular ion a were present, indicates that a undergoes considerable rearrangement even within the short time interval 3 × 10^{-11} sec.

Consider now the m/e 41 (M − CD$_2$H) fragment. The relative intensity rises from 18% at 3 × 10^{-11} sec to reach a maximum of 21% at 6 × 10^{-11} sec. The maximum is obvious in Figure 5. Thereafter the relative intensity declines toward the statistical value of 11%. The fragment m/e 41 (M − CD$_2$H) is formed only from the isomer b according to our mechanistic scheme. A maximum in the relative intensity of m/e 41 (M − CD$_2$H) implies a maximum in the proportion of b in the isotopic mixture. The initial field ionization forms the molecular ion a. The rate constant 6k for the rearrangement of a to b is three times greater than the rate constant 2k for the conversion of b to c and six times greater than the rate constant k for the reverse reaction b → a. At short times when the intensity of a is high and that of b is low (at very short times we can neglect c), the rate of formation of b will considerably exceed its rate of destruction. It must be expected that the relative intensity of b will rise rapidly and exceed the statistical value. There will come a time when the rate of formation of b, which depends on the intensity of a, will no longer exceed the rate of destruction of b, which depends on the intensity of b itself. The relative intensity of b will be at a maximum at that time[38] and

(37) It is evident (Table I) that the progress of the relative intensities of the fragment ions toward the statistical figures is very similar for the two deuterated species. If there were a significant isotope effect favoring hydrogen transfer over deuterium transfer, we would expect 1 to proceed to randomization more rapidly than 2 (see Schemes I and II). We conclude therefore that any kinetic isotope effect is small. Lack of kinetic isotope effects is consistent with the proposed mechanism which can be seen as having a highly symmetric transition state.

(38) It is possible to analyze the situation at the time 6 × 10^{-11} sec when the maximum occurs. We neglect isotope effects on the frag-

decline thereafter to the statistical value. Consider now m/e 42 (M − CDH$_2$). At no time of the order of 10^{-11} or 10^{-10} sec does the relative intensity exceed the statistical value 54%. The relative intensity rises steadily from 18% at 3 × 10^{-11} sec to 48% at 7 × 10^{-10} sec. That the relative intensity of m/e 42 (M − CDH$_2$) remains below the statistical value at all times of the order of 10^{-11} and 10^{-10} sec is readily rationalized on the basis of Scheme I. The fragment is formed from the isomer d and to a lesser extent from the isomer c. Neither c nor d can be formed directly from a, and d cannot be formed directly from b. The formation of c and d from the molecular ion a demands a minimum of two and three reactions, respectively. Given that several rearrangements must occur before fragmentation to m/e 42 (M − CDH$_2$) is possible, it is reasonable that the relative intensity of m/e 42 (M − CDH$_2$) should rise to the statistical value much more slowly than m/e 41 (M − CD$_2$H). The rather sharp bend in the m/e 42 (M − CDH$_2$) curve in Figure 5b at about 9 × 10^{-11} sec is unexpected and not readily explicable. We note, however, that the corresponding curves (Figure 6b) for 2-methyl-d_3-propane-$3,3,3$-d_3 are much smoother.

We have shown that reaction Schemes I and II involving 1,3 allylic hydrogen shifts are consistent with the kinetic data. There are reactions other than 1,3 shifts which might conceivably explain the kinetic results. Successive 1,2 shifts are conceivable, but seem unlikely to be responsible for the observed rearrangement. We suggest that 1,2 shifts lead instead to fragmentation and we discuss this possibility below. A second conceivable explanation for the kinetic results involves rearrangement via methylcyclopropane-type intermediates. We dismiss this explanation on two grounds. The heat of formation of methylcyclopropane ion is some 30 kcal/mol higher than that of 2-methylpropene ion.[39] Secondly, if methylcyclopropane species were formed, we would have expected them to be detected in the experiments of Lias and Ausloos.[19] The evidence in fact suggests that methylcyclopropane ions isomerize to 2-methylpropene and 2-butene structures. Finally "scrambling" mechanisms have been envisaged to explain H–D randomization.[40] A mechanism (eq 2) of this type would, however, be in-

mentation. We can write on the basis of Scheme I

$$[m/e\ 41] = {}^1\!/_2[b] \qquad (i)$$

$$[m/e\ 42] = {}^1\!/_2[c] + [d] \qquad (ii)$$

$$[m/e\ 43] = [a] + {}^1\!/_2[b] + {}^1\!/_2[c] \qquad (iii)$$

$[m/e\ 41]$, $[m/e\ 42]$, and $[m/e\ 43]$ are the relative intensities of these ions expressed as $percentages$ and can be obtained from Figure 6. [a], [b], [c], and [d] are the $percentage$ compositions of the isotopic mixture at 6 × 10^{-11} sec and $for those parent ions with internal energy so as to lose methyl at$ 6 × 10^{-11} sec. We can write one more equation

$$\frac{d[m/e\ 41]}{dt} = {}^1\!/_2\frac{d[b]}{dt} = {}^1\!/_2(6k[a] + k[c] − 3k[b]).$$

At 6 × 10^{-11} sec, when m/e 41 (M − CD$_2$H) is at a maximum, it is a good approximation that d[m/e 41]/dt = 0, so that

$$6[a] + [c] − 3[b] = 0 \qquad (iv)$$

Solving these four equations (eq i–iv) gives [a] = 17%, [b] = 42%, [c] 24%, and [d] = 17%. Thus, at 6 × 10^{-11} sec, some 80% of the molecular ions a have rearranged to b. Some 40% of the 80% have rearranged still further to c and then to d.

(39) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, $Nat.\ Stand.\ Ref.\ Data\ Ser.,\ Nat.\ Bur.\ Stand.,$ 26, 260 (1969).

(40) A. N. H. Yeo and D. H. Williams, $J.\ Amer.\ Chem.\ Soc.,$ 91, 3582 (1969).
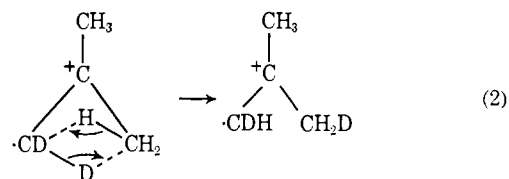
consistent with the kinetic results, since the maximum in the relative intensity of m/e 41 (M − CD$_2$H) at short times (Figure 5b) could not be readily explained. The kinetic results are in fact the first good evidence $against$ the occurrence of processes in which pairs of hydrogen (deuterium) atoms within a molecule freely exchange positions.

The kinetic results raise some interesting questions concerning the orbital structure of the reactant radical-ion and the mechanism of its fragmentation to lose methyl. We assume that we can restrict our discussion to the ground electronic state corresponding to ionization of a π electron. The possibility exists that the open shell retains the delocalized characteristics of the pristine π orbital in the neutral molecule, in which case the 1,3 shift is a sigmatropic reaction. Orbital symmetry considerations[41] demand that 1,3-sigmatropic shifts be antarafacial. Perhaps the 1,3 shift in the 2-methylpropene radical-ion does occur antarafacially. It is, however, unlikely that the analogous 1,3 shift in the cyclohexene radical-ion occurs antarafacially.[18] There are a number of reports of 1,3-sigmatropic rearrangements occurring with stereochemistry forbidden by orbital symmetry.[41b] One explanation[41b,c] offered for the occurrence of such rearrangements is that they are not truly concerted but rather proceed via an intermediate. It seems unlikely, however, that an intermediate would be involved in the 1,3 shift in the 2-methylpropene radical-ion. Possibly the 1,3 shift is not a sigmatropic reaction. Perhaps following ionization, the charge is localized on the central carbon to produce a tertiary carbonium ion [see eq 3].
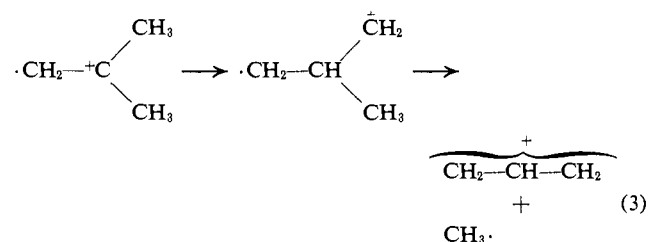
The odd electron is localized on C$_1$ to produce a primary radical site. Such a planar model structure should be energetically favorable, since the charge can be stabilized by interaction with orbitals of the methyl and methylene groups. In valence bond language the charge is stabilized by hyperconjugation. There would presumably be the same hindered internal rotation about all three C–C bonds. The 1,3 shift now corresponds to a 1,3 radical-induced rearrangement, numerous examples of which are well documented.[12] Orbital symmetry is conserved. There is now the question of why CH$_3$· is eliminated, representing as it does, formally at least, a vinylic cleavage. We suggest that the driving force is

(41) (a) K. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1971, p 114; (b) J. A. Berson, $Accounts\ Chem.\ Res.,$ 5, 406 (1972); (c) H. E. Zimmerman, $ibid.,$ 5, 393 (1972); (d) J. E. Baldwin, A. H. Andrist, R. K. Pinschmidt, Jr., $ibid.,$ 5, 402 (1972).

formation of the unusually stable allyl carbonium ion. Convincing support for this suggestion can be marshalled from the appearance potential measurements of Lossing.[42] Formation of the allyl ion implies a 1,2-hydrogen shift [see eq 3]. Such shifts within carbonium ions are well documented.[11] We now have the attractive picture of a highly symmetric planar radical-cation in which hydrogens move rapidly around the peripheral carbons by radical-induced 1,3 shifts. Competing with the radical reaction is a charge-induced 1,2 shift which leads to fragmentation. Admittedly, so far the model is speculative; however, the model contains within it a solid explanation for a baffling discrepancy between measurements by Lossing[42] and certain other measurements by Franklin and colleagues.[43] Lossing, by two separate methods, one being a direct measurement of the ionization potential, estimated the heat of formation of the allyl ion to be 226 kcal/mol. Franklin and colleagues[43] estimated the heat of formation of $C_3H_5^+$ from 2-methylpropene to be 214 kcal/mol by measurements of appearance potential and kinetic energy releases during fragmentation. The disagreement is remarkable, since there is excellent agreement between the two sets of estimations for the heat of formation of $C_3H_5^+$ from 1-butene. It appears that Franklin and coworkers have overcorrected for energy release.[43] Franklin and coworkers assume that the kinetic energy release during fragmentation originates solely from excess energy above the activation energy. This is often a safe assumption for direct bond cleavages, but is rarely valid for rearrangements since these tend to have *reverse* activation energies contributing to kinetic energy release.[44] If loss of methyl from the 2-methylpropene radical-ion is concerted with a 1,2-hydrogen shift, the reaction might be expected to have a reverse activation energy. The measured kinetic energy release would not originate solely from excess energy and use of the formula of Haney and Franklin,[45] $\bar{\epsilon}_t = E^*/\alpha N$, would be unreliable. Under these circumstances it is likely that the correction to the appearance potential would be excessive and would lead to a value for the heat of formation which was too low. We suggest that this is the origin of the discrepancy between the two estimations[42,43] of the heat of formation of $C_3H_5^+$ from 2-methylpropene.

Assuming our mechanistic model to be correct, the results provide information as to the relative activation energies and entropies of a 1,3 radical hydrogen shift as opposed to a 1,2 carbonium ion hydrogen shift. At 6×10^{-11} sec, for example, there has on average been between one and two 1,3 shifts prior to a 1,2 shift leading to fragmentation. In general the 1,3 shifts compete more effectively with the 1,2 shifts at longer times. This implies that the 1,3 shift has the lower activation energy but also a lower activation entropy (*vide infra*).

Reactions Induced by Electron Impact. The major objective of this part of the discussion is to determine to what extent the reactions induced by FI outside of the very high field (*i.e.*, times a few $\times 10^{-11}$ sec) resemble those induced by EI. The quasiequilibrium theory[36] assumes as its major premise a statistical distribution of internal energy among the internal degrees of freedom regardless of how that energy is imparted to the molecule. If this were actually true, the same reactions would be induced by both FI (at times a few $\times 10^{-11}$ sec) and EI (at the same times); only the relative amounts of the various reactions would differ on account of differing amounts of internal energy. Consider the 16 eV mass spectrum of 2-methylpropene (Figure 7). The major fragment is m/e 41 (M — CH_3) at an intensity of 10% relative to the molecular ion. The major fragment following FI is also m/e 41 (M — CH_3). The intensity of the fragment formed between 3×10^{-11} and 5×10^{-6} sec following FI is 1% relative to the molecular ion. The figure is arrived at by integrating[18] the curve in Figure 8. The higher degree of fragmentation following 16 eV EI can be attributed to a greater amount of excitation energy imparted during the ionization process. The fragment m/e 40 (M — CH_4) occurs at an intensity of $\sim 1\%$ in the 16 eV EI mass spectrum (too low an intensity to be included in Figure 7) and at an intensity of $\sim 0.1\%$ following FI.

Consider the EI mass spectra of the deuterated compounds (Figure 7). It is evident that considerable rearrangement takes place prior to fragmentation. The fragment intensities for the loss of methyl (Table I) deviate from the values calculated for complete H–D randomization. The intensities of m/e 43 (M — CH_3) with **1** and m/e 44 (M — CD_3) with **2** exceed their calculated values, whereas the intensities of m/e 42 (M — CDH_2) fall below their calculated values. The intensities of m/e 41 (M — CDH_2) with **1** and m/e 46 (M — CDH_2) with **2** slightly exceed their calculated values. These deviations from calculated values can be assumed to result from that fragmentation occurring prior to the time when H and D are completely randomized. This being so, we conclude that at times prior to H–D randomization following EI, m/e 43 (M — CH_3) from **1** and m/e 44 (M — CD_3) from **2** are formed at intensities in excess of their calculated values, but that m/e 42 (M — CDH_2) from **1** and m/e 45 (M — CD_2H) from **2** are formed at intensities less than their calculated values. At these times the fragments m/e 41 (M — CD_2H) from **1** and m/e 46 (M — CDH_2) from **2** are formed at intensities slightly in excess of the calculated values. These *deduced* trends for the fragment intensities at times prior to H–D randomization in the case of EI exactly parallel the trends *measured* in the case of FI (Table I). The correspondence between EI and FI for the m/e 41 (M — CDH_2) from **1** and m/e 46 (M — CDH_2) from **2** intensities is particularly convincing. We suggest that the reaction Schemes I and II proposed for FI are equally valid for 16 eV and possibly 50 eV EI. We suggest therefore that EI induces rapid 1,3-hydrogen shifts in the same manner as FI. Comparison of the 16 eV and 50 eV EI mass spectra of **1** and **2** (Figure 7) shows that there is less H–D randomization at the higher electron energy (Table I), *i.e.*, fewer 1,3-hydrogen shifts occur prior to fragmentation. Raising the electron energy, therefore, enhances the rate of the fragmentation relative to that of the rearrangement.[46] This would indicate that the 1,3-hydrogen shift has both

(42) F. P. Lossing, *Can. J. Chem.*, **50**, 3973 (1972).

(43) D. K. Sen Sharma and J. L. Franklin, *J. Amer. Chem. Soc.*, **95**, 6562 (1973).

(44) E. G. Jones, J. H. Beynon, and R. G. Cooks, *J. Chem. Phys.*, **57**, 2652 (1972).

(45) M. A. Haney and J. L. Franklin, *J. Chem. Phys.*, **48**, 4093 (1968).

(46) The effects of electron energy on H–D randomization processes have been discussed previously; see A. N. H. Yeo, R. G. Cooks, and D. H. Williams, *Chem. Commun.*, 1269 (1968).

a lower activation energy and a lower activation entropy (or frequency factor[36]) than the fragmentation to lose methyl.[47] The same conclusion can be established[18] somewhat more securely from, and is implicit in, our discussion of the FIK results (Figures 5 and 6).

It has been common practice among mass spectroscopists to refer to all such H–D rearrangement as we have been discussing as "scrambling." The term "scrambling" seems to hold a mechanistic implication, namely that H and D atoms move and exchange positions in a random manner. This is not the case with the 2-methylpropene ion. We suggest, mainly on the basis of FIK results,[17,18,47–49] that with all functionalized aliphatic ions the predominant reactions leading to H–D randomization are *specific* and *definable hydrogen shifts*. The nature of the shifts will depend very much on the nature of the molecule; e.g., shifts in alkene ions[17,18] bear little relationship to those in ketone ions.[48] In such a situation the term "scrambling" is seriously and objectionably misleading. The mechanistic implication is false and there is the false suggestion of some common characteristics or links among processes which are actually widely disparate. We suggest therefore that the use of the term "scrambling" be discontinued. In those cases where the rearrangements cannot be identified more precisely, it seems sufficient to refer to "rearrangements leading to H–D randomization."

Conclusion

The study of this relatively simple system establishes with some degree of certainty that 1,3 allylic hydrogen shifts are facile and rapid unimolecular gas-phase reactions of the 2-methylpropene radical-cation. This is an important result in itself. Moreover, similar 1,3 allylic hydrogen shifts must be expected to occur in other alkene radical-cations. This knowledge will be a considerable asset in unraveling the complexities of the chemistry of such reaction systems. Further FIK experiments are in progress with butenes and other alkenes.

(47) For a discussion of the usefulness of the concepts of energy and entropy of activation in understanding unimolecular reactions of (radical-) cations and in particular FIK results, see P. J. Derrick and A. L. Burlingame, *Accounts Chem. Res.*, in press.

(48) P. J. Derrick, A. M. Falick, A. L. Burlingame, and C. Djerassi, *J. Amer. Chem. Soc.*, **96**, 1054 (1974).

(49) P. J. Derrick, A. M. Falick, and A. L. Burlingame, *J. Chem. Soc., Perkin Trans. 2*, submitted for publication.

Mass Spectrometry in Structural and Stereochemical Problems. CCXLIII.[1] Functional Group Interaction. Unusual Fragmentations of Amides as Exemplified by Bipiperidyl Alkaloids[2]

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Abstract: This study deals with the mass spectrometric behavior of the bipiperidyl alkaloids of the 1-acetyl-1,2,3,4-tetrahydro-5-(2-piperidyl)pyridine (ammodendrine) (**1**) type. This alkaloid and its acyl analogs (**10,14–16**) display prominent peaks due to amide bond cleavage and several rearrangement ions. The most unusual fragmentation involves loss of hydroxyl from these molecules, which is unprecedented among amides. Other bipiperidyl alkaloids discussed are N'-methylammodendrine (**9**), adenocarpine (**10**), hystrine (**11**), and N-acetylhystrine (**12**). The mass spectrum of N'-acetylammodendrine (**13**) shows loss of water as its base peak at both 70 and 15 eV. This unexpected reaction as well as the hydroxyl loss and others were investigated using high-resolution mass spectrometry, metastable defocusing, and deuterium labeling. Plausible rationalizations are presented for these reactions which are consistent with all isotopic labeling studies.

I n recent years one of the main activities in this laboratory has been the study of the mass spectra of di- and polyfunctional molecules.[3] As the mass spectral fragmentation patterns of monofunctional molecules are well understood, it becomes important to determine the extent to which functional groups within a molecule interact to produce fragmentations not characteristic of either isolated functionality. In this context we now wish to report some unusual results encountered in the mass spectra of some bipiperidyl alkaloids, represented by ammodendrine (**1**).

During the course of an investigation into the alkaloidal constituents of a local plant, *Lupinus formosus*,[4] we isolated a compound of molecular formula

(1) For the preceding paper, see D. H. Smith, C. Djerassi, K. Maurer, and U. Rapp, *J. Amer. Chem. Soc.*, **96**, 3482 (1974).

(2) Financial assistance by the National Institutes of Health (Grant No. AM 04257) is gratefully acknowledged.

(3) See, for example: (a) M. Sheehan, R. Spangler, M. Ikeda, and C. Djerassi, *J. Org. Chem.*, **36**, 1776 (1971), and references cited therein; (b) R. J. Liedtke and C. Djerassi, *J. Org. Chem.*, **37**, 2111 (1972); (c) J. R. Dias and C. Djerassi, *Org. Mass Spectrom.*, **6**, 385 (1972).

(4) W. L. Fitch, P. M. Dolinger, and C. Djerassi, submitted for publication in *J. Org. Chem.*