

2,2-Dimethylindanone-¹⁸O, 2,2-Dimethylindanone (0.11 g) in 5.0 mL of aniline was refluxed for 12 h with 0.20 mL of BF₃·Et₂O. The resulting crude solid was recrystallized from ether to yield 0.08 g of 2,2-dimethylindan-1-phenylimine: mp 43–46 °C; IR (CHCl₃) 2960, 2930, 1658, 1592, 1483, 1464, 1301, 1165, 1005, 996 cm⁻¹; NMR (CDCl₃) δ 1.37 (s, 6), 2.99 (s, 2), 6.50 (d, 2), 6.85 (m, 3), 7.10 (t, 1), 7.30 (m, 4). This phenylimine (0.0543 g) and 0.01 mL of 99% H₂¹⁸O were treated with dry HCl until the solid began to go into solution and heated in a 130 °C oil bath for 0.5 h. The solution was extracted with a 1:1 mixture of cyclohexane–chloroform and the solvents were removed under vacuum to yield 0.0375 g of 2,2-dimethylindanone-¹⁸O; IR (CHCl₃) 1675, 1608, 1290, 990 cm⁻¹.

Note Added in Proof. Since the present manuscript was accepted, very closely related theoretical studies were reported by S. B. Piepho, E. R. Krausz, and P. N. Schatz (*J. Am. Chem. Soc.*, **100**, 2996 (1978)). These authors have applied the same sort of approach to describing vibronic structure of the optical intervalence transition for the special case of only one dependent coordinate.

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Fragmentations of Alkane Molecular Ions

Peder Wolkoff and John L. Holmes*

Contribution from the Chemistry Department, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4. Received March 23, 1978

Abstract: The appearance energies of daughter ions for the major fragmentations of butane and methylpropane and those for loss of CH₃⁺ and CH₄ from propane, pentane, methylbutane, and hexane have been measured. These reactions for molecular ions of low internal energy content (rate constants in the range 10⁵–10⁷ s⁻¹) have been investigated by measurements of the relative abundances of metastable peaks and their accompanying translational energy releases. The deuterium-labeled species propane-2,2-²H₂, butane-1,1,1,4,4,4-²H₆, butane-2,2,3,3-²H₄, butane-1,1,1,2,2-²H₅, and methyl-²H₃-propane-2-²H₁ have also been examined. The accumulated information for loss of methyl from straight-chain alkane molecular ions indicates that this reaction proceeds largely by loss of a terminal methyl group, accompanied by a concerted H atom shift to yield a secondary carbonium ion. Loss of methyl from within the hydrocarbon chain may proceed from a molecular ion which has isomerized to a methyl-branched alkane or by a concerted extrusion of methylene together with an adjacent H atom, again producing a secondary carbonium ion. Hydrogen atoms are not "scrambled" in either of these processes. It is proposed that the eliminations of methane from metastable molecular ions of butane and methylpropane both yield [cyclopropane]⁺ as the daughter ion. The losses of CH₄, CH₃D, and CD₃H (metastable peak abundance ratios 26:15:10) from butane-2,2,3,3-²H₄ were significantly different from those for the tetradeuterated isomer, methyl-²H₃-propane-2-²H₁, where the ratios 78:18:~1 were observed. These results are compatible with the retention of skeletal structure in the linear alkane molecular ions. However, the metastable molecular ions of butane have a higher energy content than those of methylpropane and so isomerization of the former to the latter prior to fragmentation cannot be ruled out.

Introduction

In 1945 Hipple, Fox, and Condon examined the normal mass spectrum of butane¹ and observed diffuse peaks therein; these they interpreted as arising from decompositions of ions in the field-free region preceding the analyzer (the magnet). Since then there have been many investigations directed toward identifying the decomposition mechanisms of the butane molecular ion and of alkane molecular ions in general.^{2,3}

A 1973 review² states that alkane molecular ions inter alia decompose via rearrangements, which possibly are accompa-

nied or preceded by partial or complete loss of the positional identity of the hydrogen atoms—a well-established feature of the chemistry of alkene molecular ions and alkyl cations.³ However, a survey of the recent literature (cf. ref 3) reveals that it remains to be established whether alkane molecular ions isomerize prior to decomposition, rearrange during decomposition, or indeed whether H atoms do lose their positional identity prior to fragmentation (for detailed discussion cf. ref 4–7). Many techniques, including isotopic labeling, have been used to interpret the mass spectra of the simplest class of or-

Table I. Thermochemical Data for $[M - CH_3]^+$ Ions from Some Alkane Molecular Ions

| | ΔH_f , kcal/ mol | AE ($[M - CH_3]^+$), ^a eV | ΔH_f ($[M - CH_3]^+$), kcal/mol | ΔH_f for sec ion formation, ^b kcal/mol |
|---------|--------------------------------|-------------------------------------------|----------------------------------------------|--------------------------------------------------------------------|
| pentane | -35.00 | 11.06 | 186 | 183 |
| hexane | -39.96 | 11.05 | 181 | 179 (2-pentyl) |
| heptane | -44.89 | 10.8 ± 0.2 | 170 | 173 (2-hexyl) |
| octane | -49.82 | 10.9 ± 0.1 | 167 | 168 (2-heptyl) |

^a Reference 11. ^b F. P. Lossing and A. Maccoll, *Can. J. Chem.*, **54**, 990 (1976).

ganic compounds, alkanes. However, the information extracted from chosen models has been too complex to permit the unraveling of detailed mechanisms of decomposition. For example, metastable peak characteristics,⁸ field ionization mass spectrometry,⁹ and collision activation mass spectrometry⁴ of isomeric octanes have indicated that their molecular ions retain their structural integrity prior to decomposition. The opposite conclusion was reached by Loudon et al.¹⁰ They concluded from measurements of the appearance energies of their respective $[M - CH_3]^+$ ions, from all 18 C_8H_{18} isomers, that the daughter ions must have a tertiary structure, irrespective of the precursor molecule. This was interpreted in terms of "flexures", a series of isomerization steps involving CH_2 extrusions and producing species capable of forming a tertiary daughter ion by a simple bond fission. Recent photoionization data¹¹ clearly indicate that for pentane, hexane, heptane, and octane, secondary carbonium ions rather than tertiary ions are generated by loss of a methyl group from the molecular ions (see Table I). Liardon and Gaumann¹² concluded from their observations of methyl and methane loss from the molecular ions of deuterium-labeled hexanes that two different mechanisms were independently operating. One was the straightforward loss of a terminal methyl group and the other involved the loss of methyl from within the chain. Similar results obtained by Corolleur et al.¹³ were interpreted differently, in terms of alkyl group and hydrogen atom migrations. From the foregoing, it is evident that the unimolecular decompositions of this class of organic compounds are poorly understood.

The normal mass spectra of butane and methylpropane are very similar and thus may arise via a common reacting configuration for $[C_4H_{10}]^+$. (Such interconversions are indeed reasonable; e.g., butane is readily catalytically isomerized to methylpropane in the presence of aluminum chloride¹⁴).

The purpose of this work is to try to answer the following questions: Do alkane molecular ions isomerize prior to fragmentation? What daughter ion structures are produced? Furthermore, how does the observed apparent (partial) loss of positional identity of hydrogen atoms come about?

Butane and methylpropane were chosen as the model compounds in this study. Deuterium labeling and other techniques were used to establish the decomposition modes and the structures of the daughter ions. The latter also were investigated by thermochemical measurements (ionization and appearance energies), which were made for us by Dr. F. P. Lossing at the National Research Council of Canada with energy selected electrons using an apparatus and technique described in detail elsewhere.¹⁵ Metastable peak characteristics (i.e., observations of ions with lifetimes of a few microseconds which decompose in the first field-free region—that which precedes the electric sector—in the A. E. 1.-G. E. C. MS902S mass spectrometer) were also examined in detail.

Results and Discussion

Energetics. The most recent thermochemical data for the primary fragmentations of butane and methylpropane are

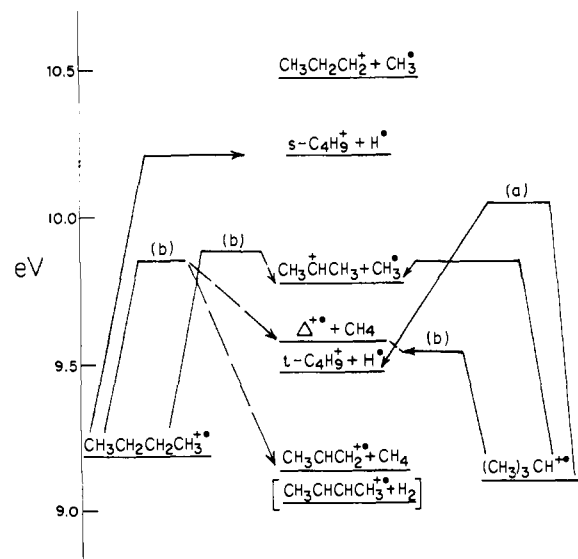


Figure 1. Energy diagram for the primary fragmentations of butane and methylpropane. The selected ΔH_{f298} values from ref 11 have been used for the thermochemical levels; note that the level for $[c-C_3H_6]^+ + CH_4$ is an upper limit. The lines linking the thermochemical levels relate to measured appearance energies (AE) obtained either from ref 11 or as indicated. (a) AE 11.45 ± 0.05 eV; energy selected electrons, this work. (b) Averaged values, ref 11 and AE (this work; see Table II).

shown in Figure 1. Although elimination of H_2 is the process with the lowest energy requirement, there is no evidence that such a reaction takes place. The agreement between appearance energies (AE) derived from photoionization spectra (PI) and energy-resolved electron impact (EM) measurements is very satisfactory (see also Table II). The reactions illustrated in Figure 1 will be discussed separately.

Loss of H^+ from $[C_4H_{10}]^+$. For methylpropane the AE for $[C_4H_9]^+$ is 0.56 eV above the calculated minimum for $[tert-butyl]^+$ generation (see Figure 1). Thus this reaction can only yield the *tert*-butyl cation at threshold. The fragmentation is therefore accompanied by an appreciable kinetic or competitive shift (or possibly a reverse activation energy).

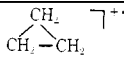
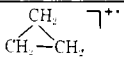








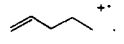
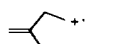
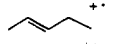
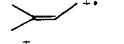

The metastable peak for this reaction is weak and the energy release, calculated from the width of the peak at half-height, $T_{0.5} \sim 0.007$ eV, is comparable with that for the loss of H from the propane molecular ion.¹⁸ A very large isotope effect has been reported for this metastable fragmentation for $(CH_3)_3CD$.¹⁹

For butane the reaction proceeds with an AE close to the calculated threshold for the formation of the 2-butyl cation. No metastable peak was observed for this process, indicating that molecular ions decomposing by this reaction have lives of less than $\sim 0.1 \mu s$.

Loss of CH_3^+ from $[C_4H_{10}]^+$. For both molecules this reaction proceeds within 0.05 eV of the calculated threshold for the most stable product, the 2-propyl cation. Thus the butane molecular ion must rearrange either prior to or during the loss of a methyl radical. The loss of CH_3^+ from methylpropane, which also proceeds at the calculated AE, apparently involves only a simple bond cleavage, as indicated by deuterium-labeling experiments.²⁰ In the case of butane a strong (first field-free region) metastable peak was observed for loss of CH_3^+ and the energy release, $T_{0.5} = 0.014$ eV, is of similar magnitude to that observed for methyl loss from the isomeric $[C_4H_8]^+$ ions.²¹ For methylpropane only a very weak peak is observed, $T_{0.5} \sim 0.025$ eV; methyl loss here competes unfavorably with methane elimination, which has an activation energy lower by 0.3 eV.

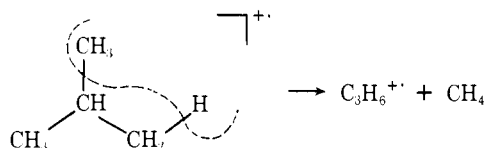
Methane Loss from $[C_4H_{10}]^+$. For ions of low internal energy it has been proposed that methylpropane loses methane

Table II. Loss of CH₄ and CH₃· from Alkanes

| compd | AE, eV | | daughter ion | excess energy, eV ^b | T _{0.5} , eV | M*CH ₃ /M*CH ₄ |
|---------------|--------------------------------------------|-----------------------------------------------------------------|---------------------------------------------------------------------------------------------------|--------------------------------|-------------------------------------------------------------------------------|----------------------------------------------------------------|
| | CH ₄ loss | CH ₃ loss | | | | |
| propane | 11.52 ^a | | C ₂ H ₄ ⁺⁺ | 0-0.1 | 0.016 ± 0.001 (T _{av} = 0.048) | |
| | 11.72 ¹⁶ ~11.6 ²³ | 11.8 ²³ 11.9 ¹⁶ | C ₂ H ₅ ⁺ | 0 | | |
| butane | 11.15 ^a | |  ⁺⁺ | 0.26 | 0.022 ²⁶ | |
| | 11.18 ¹⁶ 11.16 ¹⁷ | | CH ₃ CHCH ₂ ⁺⁺ | 0.69 | 0.021 ± 0.001 (T _{av} = 0.064) | 1.22 ^e 1.25 ²⁸ |
| | | 11.2 ^a 11.18 ¹⁶ 11.19 ¹⁷ | CH ₃ ⁺ CHCH ₃ | 0.1 | 0.016 ± 0.001 (T _{av} = 0.045) [0.020 ± 0.005 eV] ^d | 0.64 ²⁹ |
| methylpropane | | |  ⁺⁺ | 0 | | |
| | 10.91 ^a 10.93 ¹⁷ | | CH ₃ CHCH ₂ ⁺⁺ | 0.43 | 0.014 ± 0.0007 (T _{av} = 0.042) | <0.2 ^e <0.33 ²⁸ ~0.3 ²² |
| | | 11.23 ¹⁷ | CH ₃ ⁺ CHCH ₃ | 0.1 | vw ~0.025 | |
| pentane | | |  ⁺⁺ | -0.13 | | |
| | 11.00 ^a 10.93 ¹⁷ | |  ⁺⁺ | 0.52 | 0.037 ± 0.002 (T _{av} = 0.11) | 0.60 ^e |
| | | |  ⁺⁺ | 0.65 | | |
| | | |  ⁺⁺ | 1.21 | | |
| | | 11.00 ¹⁷ 10.98 ¹⁶ |  ⁺ | 0 | 0.014 ± 0.002 (T _{av} = 0.035) | |
| methylbutane | 10.7 ¹⁷ | |  ⁺⁺ | 0.13 | 0.030 ± 0.002 (T _{av} = 0.090) | <0.1 ^e |
| | | 11.1 ¹⁷ |  ⁺ | 0.1 | | |
| hexane | 11.00 ¹⁷ | |  ⁺⁺ | 0.35 | 0.042 ± 0.003 | |
| | | |  ⁺⁺ | 0.78 | | |
| | | |  ⁺⁺ | 1.30 | (T _{av} = 0.125) | 1.4 ^e |
| | | |  ⁺⁺ | 1.47 | | |
| | | |  ⁺⁺ | 1.82 | | |
| | | 11.05 ¹⁷ |  ⁺ | 0.1 | 0.016 ± 0.002 (T _{av} = 0.041) | |

^a Values from this work, ±0.05 eV.¹⁵ ^b AE (obsd) - AE (calcd from ref 11). ^c F. P. Lossing and A. Maccoll, *Can. J. Chem.*, **54**, 990 (1976). ^d G. Khodadadi, R. Botter, and H. M. Rosenstock, *Int. J. Mass Spectrom. Ion Phys.*, **3**, 397 (1969). ^e Metastable peak areas, this work.

by a 1,2-elimination.^{20,22} The tertiary H atom is not involved, indicating the absence of positional exchange between H atoms. However, in spite of this apparently simple mechanism



the reaction proceeds with an AE corresponding *not* to the formation of [propene]⁺⁺, the product of lowest energy, but (within experimental error) to the calculated threshold for the cyclopropane molecular ion; see Figure 1. The reaction produces an intense metastable peak with T_{0.5} = 0.014 eV.

For butane the daughter ions *m/e* 43 and 42 (losses of CH₃·

and CH₄) and the corresponding metastable peaks¹⁶ all have the same AE (within experimental error). This confirms that the metastable peaks indeed arise from the threshold reaction. Thus (see Figure 1) decomposing butane ions are at least 0.28 eV "hot" with respect to [cyclopropane]⁺⁺ as daughter ion or contain 0.69 eV excess energy with respect to [propene]⁺⁺.

These observations show that either [C₃H₆]⁺⁺ daughter ion may be generated at threshold from each C₄ alkane. The deuterium-labeling experiments of Derrick et al.^{20,22} on methylpropane are, however, most simply interpreted by proposing that [CH₃CHCH₂]⁺⁺ is produced from methylpropane. Note that the suggested 1,2-molecular elimination depicted above is a symmetry-forbidden process and thus may have a prohibitively large activation energy.

It is useful at this stage to extend the discussion to include

observations of the energetics of some homologous alkanes, where it has been reported^{16,17} that the photoionization AE values for loss of CH₃[•] and CH₄ from butane, pentane, and hexane are identical (within experimental error) for each hydrocarbon. These results, together with new thermochemical data and metastable peak observations, are presented in Table II.

Behavior of Propane. Propane and deuterium-labeled propanes have recently been studied by threshold photoelectron-photoion coincidence mass spectrometry.²³ It was found that, although the predominant methane loss from [CH₃CD₂CH₃]⁺ consisted of CH₄, the eliminations of CH₃D and CH₂D₂ were not negligibly small. This result conflicts with the observations of Lifshitz and Shapiro,²⁴ who had shown that a metastable peak only for the former reaction—presumably a 1,2-elimination—could be observed in the microsecond time frame. We have reexamined this compound and find that the metastable peak for CH₄ loss is at least 250 times as intense as those for loss of CH₃D or CH₂D₂ (relative abundances ~0.8 and ~0.8, respectively), essentially in agreement with Lifshitz and Shapiro. The signals we observed for the latter two methane losses cannot have arisen from isotopic impurities; the labeled propane contained better than 98% CH₃CD₂CH₃; thus, for example, the contribution from ¹³CH₄ loss from [¹³CC₂H₇D]⁺ would be small indeed (<0.06). From Stockbauer and Inghram's experiments,²³ the AE values for the mixed methane losses were about 0.1 eV higher than that for CH₄ loss. The AE values for *m/e* 30, 29, and 28 from CH₃CD₂CH₃ have been measured for us by Dr. F. P. Lossing using energy-selected electrons and a minicomputer for data accumulation.¹⁵ The values for *m/e* 28 and 29 were the same (11.76 ± 0.05 eV), slightly but significantly higher than that for *m/e* 30, 11.52 ± 0.05 eV. (Compare 11.43 eV from the results of Stockbauer.²³) At 1 V above threshold the peak intensities *m/e* 30:29:28 were ~100:8:9, also in fair agreement with Stockbauer's observations²³ and confirming that the latter pair of label-mixing reactions is of significance. We conclude therefore, that the 1,2-elimination of methane from propane occurs within 0.15 eV of the calculated threshold for the production of [C₂H₄]⁺, 11.35 eV. The elimination reactions which involve (deuterium) atoms from the central methylene group have a slightly higher activation energy and are barely observable in the microsecond time frame. However, none of the observations supports the proposal²³ that randomization of H/D atoms precedes the CH₃D and CH₂D₂ losses. These two reactions were seen to occur with similar probabilities near threshold and the random statistical losses of CH₃D and CH₂D₂ would be in the ratio 8:3.

Daughter Ion Structures for [Alkane - CH₄]⁺ Ions. As can be seen from Table II, the number of energetically feasible daughter ion structures derived from CH₄ elimination increases rapidly with the alkane size. For example, in the case of pentane, the cyclobutane molecular ion cannot be a threshold product from CH₄ loss, but *all* the remaining [C₄H₈]⁺ isomers are thermochemically possible. Also shown in Table II are the energy releases associated with the metastable peaks for these reactions. The metastable peaks were all of the Gaussian type but of broader base than for exactly Gaussian profiles. The average energy releases, *T*_{av}, obtained from the distributions of released energies²⁵ are also given in Table II. (They are all related to the given *T*_{0.5}'s by a factor of ~3.0; compare 2.16 for an exactly Gaussian peak).

Note that for fragmentations taking place at or near the calculated thermochemical threshold (e.g., loss of CH₃[•] from butane, pentane, and hexane and loss of CH₄ from propane) similar average amounts of internal energy of the fragmenting ions are partitioned as translational energy of the products, *T*_{av} = 0.035 → 0.045 eV. Now methylpropane has similar *T* values for its methane loss. This would be unremarkable if [cyclo-

propane]⁺ were the daughter ion, but is strikingly low if [propene]⁺ were being generated with a minimum of 0.4 eV excess internal energy in addition to that necessary to attain the range of rate constants observable in metastable fragmentations.

Butane behaves similarly. The metastable peaks for [C₃H₇]⁺ and [C₃H₆]⁺ formation (which have closely similar abundances; see Table II) increase in unison up to at least 1 eV above threshold.¹⁶ Thus the rate constants for these two reactions and the internal energy contents (above threshold) for the ions fragmenting in the microsecond time frame are closely similar. However, for those ions decomposing by methane loss, the excess energy available for partitioning into product translation is greater than that available to the [M - CH₃]⁺ species by either 0.28 eV ([cyclopropane]⁺ formation) or 0.69 eV ([propene]⁺ formation). It remains to be considered which of these excess *internal* energies can best be correlated with the difference in translational energies (*T*_{av}(CH₄) - *T*_{av}(CH₃) = 0.064 - 0.045 = 0.019 eV).

Assuming that the internal energy of the decomposing ions is statistically partitioned, then the semiempirical equation of Haney and Franklin²⁷ may be applied to this problem. This equation relates the internal energy ϵ^\ddagger of fragmenting ions to the corresponding released translational energy, *T*, by the expression $\epsilon^\ddagger \approx 0.4(3n - 6)T$. For loss of CH₃[•] from butane (*n* = 14), $\epsilon^\ddagger_{av}(\text{CH}_3) \approx 0.4 \times 0.045 \times 36 \approx 0.65$ eV. Thus $\epsilon^\ddagger_{av}(\text{CH}_4) \approx 0.93$ or 1.34 eV. The calculated values for *T*_{av}(CH₄) from these two energies are ~0.065 and 0.093 eV, respectively, clearly favoring the postulate that [cyclopropane]⁺ is the daughter ion. The validity of this argument rests upon the assumption that the energy partitioning is the same for the two competing reactions. The presence of *nonstatistical* partitioning for the methane elimination cannot a priori be ruled out and thus poses an interesting dilemma. However, an experiment could provide the answer to this problem, it having been shown that [propene]⁺ and [cyclopropane]⁺ are distinguishable by ion cyclotron resonance.^{30,31} It has been shown that propene and cyclopropane molecular ions have become indistinguishable when they have sufficient internal energy to fragment (1.4 eV above the IE of cyclopropane).³² However, cyclopropane molecular ions isomerize to only ca. 15% (10⁻³ s time scale) when their internal energies are less than 0.7 eV³³ and so in the present system isomerization of [C₃H₆]⁺ ions generated near threshold would be unimportant.

Extension of the above discussion to the higher homologues is unprofitable in view of the larger number of available daughter ion structures and the resulting possibility that the methane loss metastable peaks comprise signals from several competing processes. Nevertheless, it is noteworthy that the estimated excess energies for pentane, methylbutane, and hexane, 1.22, 0.81, and 1.40 eV, respectively (calculated as above), all correspond closely to those for the production of the 2-olefin cations (1.21, 0.83, and 1.47 eV, respectively).

One final point about butane deserves careful consideration. The observed common threshold energy for methyl and methane loss could simply be explained by requiring that butane molecular ions isomerize to methylpropane prior to decomposition. This was proposed by Vestal³⁴ and by Lias et al.,³⁵ but has recently been discounted by Sunner and Szabo.³⁶ The energetic data presented in this paper are not in conflict with the isomerization hypothesis, with the exception that the H atom loss from butane might then be expected to have an AE below the threshold for the 2-butyl cation (i.e., nearer to the threshold for [*tert*-butyl]⁺ formation from methylpropane). This objection could be allayed by an appropriate kinetic argument.

Deuterium-Labeled Butanes. Some 20 years ago the normal mass spectra of some D-labeled butanes³⁷ were reported and the observations indicated that some loss of positional identity

Table III. Relative Abundances (Peak Heights) and $T_{0.5}$ Values^a (meV) of Metastable Peaks for Losses of Methyl and Methane from Labeled Butanes

| | CH ₃ | $T_{0.5}$ | CH ₂ D/CH ₄ | $T_{0.5}$ | CHD ₂ /CH ₃ D | $T_{0.5}$ | CD ₃ /CH ₂ D ₂ | $T_{0.5}$ | CD ₃ H | $T_{0.5}$ | CD ₄ | $T_{0.5}$ |
|---------------------------------------------------------------------|-----------------|-----------|-----------------------------------|-----------|-------------------------------------|-----------|-------------------------------------------------|-----------|-------------------|-----------|-----------------|-----------|
| CH ₃ CH ₂ CH ₂ CH ₃ (1) | | 16.1 | | 20.4 | | | | | | | | |
| CD ₃ CH ₂ CH ₂ CD ₃ (2) | 2.9 | 14.8 | <0.3 | | 5.6 | 21.4 | 47.3 | 18.0 | 26.7 | 20.5 | 17.5 | 18.9 |
| CH ₃ CD ₂ CD ₂ CH ₃ (3) | 45.3 | 15.3 | 25.7 | 23.0 | 15.5 | 21.7 | 3.6 | 14.1 | 9.9 | 17.8 | <0.4 | |
| CD ₃ CD ₂ CH ₂ CH ₃ (4) | 19.6 | 16.7 | 10.9 | 20.0 | 20.5 | 21.6 | 25.0 | 17.3 | 19.2 | 21.1 | 4.8 | 21.3 |

^a $T_{0.5}$ values $\pm 5\%$.

of H and D possibly took place prior to decomposition within the ion source (i.e., among ions of high internal energy content). Many other examples have appeared in the literature (cf. ref 2 and 6), where the losses of variously labeled fragments from alkane molecular ions which had been *specifically* positionally labeled with deuterium have been explained by the vague term "incomplete or partial scrambling".

We have examined the distributions of H and D among the ions produced by loss of methyl and methane from the metastable molecular ions of 1,1,1,4,4,4-hexadeuteriobutane (2), 2,2,3,3-tetradeuteriobutane (3), and 1,1,1,2,2-pentadeuteriobutane (4). The results are summarized in Table III. It is clear that the H and D atoms in labeled butanes have *not* become randomly positionally distributed prior to metastable decomposition, because, for example, 2 does not lose CH₄, and 3 does not lose CD₄.

These results are in agreement with those of Smith and Futrell,²⁹ who examined the losses of methyl and methane from the molecular ion of 1,1,1,2,2,3,3-heptadeuteriobutane in a tandem mass spectrometer. Their observations extended to longer reaction time (from 2 μ s to 4 ms) than the present work (microsecond range) and they concluded that methane elimination became the favored process (over methyl loss) at the longest reaction time (see Table II).

In the experiments on deuterium-labeled propane referred to above, the metastable peak observations showed only one major mode of methane loss. This contrasts sharply with the photoelectron-photoion coincidence studies, where H/D mixing was apparently involved.

We believe that the chief reason for this discrepancy lies in the different ion lifetimes sampled in the experiments. Observations on metastable ions correspond to all ions (irrespective of their energy contents) which have dissociation rate constants of from ca. 10^5 to 10^7 s⁻¹. The ions are thus selected by rate constant. The photoelectron-photoion coincidence experiments involve ions having selected internal energies but a much wider range of rate constants contributes to the observations.

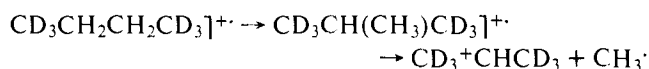
A similar but very much reduced effect can be seen in the butane system. The normalized relative abundances of m/e 44, 45, 46, 47, 48, and 49 from 2, measured at 1.3 eV above threshold (using energy-selected electrons and an apparatus which detects all ions produced up to ~ 30 μ s), were 9:11:70:5:2:3. These can be compared with the corresponding metastable peak abundances, 17:25:48:5: \sim 0:3, where only CH₂D (or CH₄) loss is suppressed.

It is evident from the results shown in Table III that the butane molecular ion must decompose by (at least) two competing mechanisms, because 2 loses CD₃[·] and CH₃[·], and CD₄ as well as CH₃D. The behaviors of 3 and 4 are analogous with that of 2. There is no evidence for the operation of any major isotope effects—the ratio methyl loss:methane loss is approximately unity for 2 and 3.

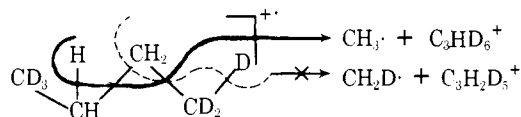
Loss of Methyl. It is clear from the results presented in Table III that "terminal" methyl loss exceeds "internal" methyl loss by a factor of ~ 15 (e.g., for 2 CH₃:CD₃ = 3: \sim 45; for 3 the ratio is \sim 45:3.5).

This observation is not compatible with the hypothesis that all butane molecular ions isomerize to [methylpropane]⁺ prior

to this decomposition. In that case CH₃[·] loss:CD₃[·] loss in 2 should be $\sim 1:2$. It is possible that the CH₃[·] loss from 2 arises wholly or partially from an isomerized molecular ion.



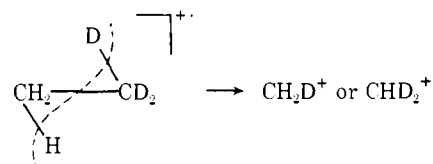
The terminal methyl loss must be accompanied by a concerted hydrogen atom shift from C-3 to C-2 in order that [2-propyl]⁺ be the daughter ion. The internal methyl loss can also be explained by the extrusion mechanism of Liardon and Gäumann.¹² Of the two detailed mechanisms for this process shown below, one can be of only minor importance because 2



loses an insignificant amount of CH₂D[·]. This can be rationalized on the basis of the extruded methylene competing for *primary* deuterium or the more labile *secondary* hydrogen.

The AE values for loss of CH₃[·] (m/e 49) and CH₂D[·] (m/e 48) from 2 were 11.30 ± 0.05 and 11.32 ± 0.05 eV, respectively, slightly but significantly above those for CD₄ loss (m/e 44), 11.15 ± 0.05 eV; CD₃H loss (m/e 45), 11.16 ± 0.05 eV; CD₃[·] (or CH₂D₂) loss, 11.18 ± 0.05 eV; and CH₃D (or CHD₂) loss, 11.18 ± 0.05 eV. Although the metastable peak for loss of CH₂D[·] was very small, the daughter ion abundance (m/e 48) was similar to that of m/e 49 at energies near to threshold, (e.g., 1.3 eV above threshold, m/e 49: m/e 48 = 3:2). Similar results were observed for 3; the metastable peak for loss of 17 daltons therefrom has a $T_{0.5}$ value corresponding to the methane elimination (CH₃D) rather than loss of CHD₂[·].

Either the above "extrusion"-type mechanism or the isomerization process can be invoked satisfactorily to explain the losses of methyl or an alkyl radical from within the hydrocarbon chain of hexacosane,³⁸ dodecane,⁶ or even saturated fatty acid esters.³⁹ In the case of dodecane-1,12-¹³C₂, where methyl loss is a minor process, CH₃[·] and ¹³CH₃[·] are lost in approximately equal amounts.⁶ The preferential loss of CH₃[·] over CD₃[·] from 1,1,1-trideuteriopentane⁴⁰ can also be explained by the participation of the internal mode of methyl elimination. Finally, the recently reported losses of CHD₂[·] and CH₂D[·] from [CD₃CH₃]⁺ need not be rationalized⁴¹ by invoking a "scrambling transition state". The reaction could proceed via



the quasi-extrusion mechanism. The results⁴¹ show that these two processes have activation energies higher by ~ 1.5 eV than that for the simple C-C fission, but they provide a significant fraction of the total methyl loss at an ionizing electron energy of 22.6 eV.

To summarize, we propose that the bulk of methyl loss from

[butane]⁺ arises from terminal CH₃[•] expulsion, together with a concerted H[•] atom shift to produce the 2-propyl cation. The "internal" methyl loss arises from *either* a methylene extrusion reaction or as part of the methyl loss (by a simple bond cleavage) from a methylpropane molecular ion. For metastable ions these reactions involve little, if any, isotope randomization. Ions of shorter lifetime (higher internal energy) do display some apparent loss of positional identity of H and D atoms.

Loss of Methane. The observations on the labeled butanes, Table III, can be rationalized by several mechanisms. 1,1-, 1,2-, and 1,3-eliminations of methane from an unrearranged molecular ion can account for the losses of CD₃H and CD₄ from **2** and CH₃D and CH₄ from **3**. Losses of CH₃D from **2** (and CD₃H from **3**) require *either* an isomerization to [methylpropane]⁺ or an extrusion reaction in which two hydrogen atoms are transferred to the departing methylene. The earlier discussion of energetic data which considered daughter ion structures, in which [cyclopropane]⁺ production from both [C₄H₁₀]⁺ isomers was proposed, leads us tentatively to favor the rearrangement mechanism. This qualitatively accounts for the losses of CH₃D, CD₃H, and CD₄ (no loss of CH₄, CH₂D₂) from **2** and CH₄, CH₃D, and CD₃H (no loss of CD₄, CH₂D₂) from **3**. If this is indeed the correct mechanism, then the observed relative abundances of the various daughter ions must be governed by isotope or other kinetic effects, since no simple quantitative interpretation of the results is feasible. As in the case of methyl loss, the metastable ions display little or no positional mixing of isotopes. Note that this lack of mixing requires that any [butane]⁺ → [methylpropane]⁺ isomerization be an irreversible process.

In order to test the isomerization hypothesis the metastable peaks for loss of methane from [CD₃(CH₃)₂CD]⁺ were examined. (Note that methyl loss from methylpropane only generates a very weak metastable peak.) Surprisingly, loss of CH₄ predominated, 78 ± 4%, loss of CH₃D comprised 18 ± 4%, while losses of CH₂D₂, 2 ± 2%, and CD₃H, 1 ± 1%, were very minor processes indeed. This somewhat unexpected result is being investigated further and will be reported in detail elsewhere. Clearly a large isotope effect is operative, having a magnitude similar to that observed for the loss of the tertiary H(D) atom.¹⁹ Observations of this kind have also been reported by Neeter and Nibbering⁴² in their studies of *tert*-butylbenzene and 4-*tert*-butylpyridine.

The present observations rule out the possibility of positional exchange among H and D atoms within the methyl groups.¹⁸

The above observations do not provide support for or against the isomerization hypothesis for butane fragmentation. For example, it could be argued that deuterium-labeled methylpropane molecular ions *having the same internal energy content as metastable "butane"* molecular ions would, by virtue of their higher energy content, display a greater loss of CD₃H—similar to that observed for **3**. The larger energy release for CH₄ loss from rearranged butane molecular ions would necessarily result from the kinetic delay effect, i.e., methylpropane ions formed by rearrangement of [butane]⁺ would require larger internal energies (than ions formed by direct ionization of methylpropane) to fragment in the metastable time frame. It could be argued that the absence of a metastable peak for CD₃H loss from [CD₃(CH₃)₂CD]⁺ is also in keeping with [cyclopropane]⁺ formation, because the daughter ions for methane losses, *m/e* 46, 45, 44, and 43, have similar abundances at low ionizing electron energies. Analogous observations on CH₃CD₂CH₃ were discussed earlier.

Summary

We conclude that the loss of a methyl radical from alkane molecular ions proceeds mostly by loss of a terminal methyl group together with some loss of "internal" methyl, either

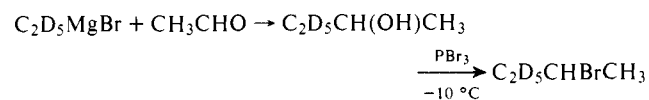
involving a simple extrusion reaction or proceeding via isomerization to a methyl-branched homologue. All processes yield a secondary carbonium ion.

We propose that the eliminations of methane from [methylpropane]⁺ and [butane]⁺ both produce [cyclopropane]⁺ as daughter ion. It is possible that [butane]⁺ isomerizes to its branched homologue prior to this fragmentation, but present data do not provide unequivocal evidence to support this hypothesis. The kinetics and mechanisms of these elimination reactions require further investigation.

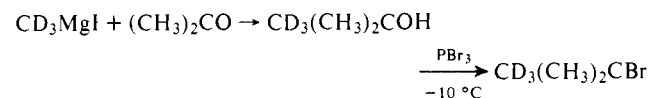
Experimental Section

Metastable peak shapes were measured at a fixed electric sector voltage by sweeping the acceleration voltage of an AEI-GEC MS 902S mass spectrometer, using conditions of good energy resolution.⁴³

Butane-1,1,1,4,4,4-²H₆ and propane-2,2,2-²H₂ were purchased from Merck Sharp and Dohme. Butane-2,2,3,3-²H₄ was prepared by reduction of 1,4-dibromobutane-2,2,3,3-²H₄ (Merck Sharp and Dohme) with lithium triethylborohydride (Aldrich).⁴⁴ Butane-1,1,1,2,2-²H₅ was prepared by reduction as above⁴⁴ of 3-bromobutane-1,1,1,2,2-²H₅, which was synthesized by the following sequences:^{45,46a}



2-(Methyl-²H₃)propane-2-²H₁ was prepared by reduction with anhydrous NiCl₂/LiAlD₄ (molar ratio 1:1)⁴⁷ of 2-bromo-2-(methyl-²H₃)propane, which was prepared as follows:^{45,46a,b}



A ¹H NMR spectrum of the bromides showed that no H/D exchange had occurred. Deuterium contents were CD₃CH₂CH₂CD₃, 99% ²H₆; CH₃CD₂CD₂CH₃, 97% ²H₄, 3% ²H₃; CD₃CD₂CH₂CH₃, 90% ²H₅, 10% ²H₄.

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Photochemistry of Bichromophoric Molecules. Photochemistry and Photophysics of 2-Methylenebenzborbornene and Related Nonconjugated Aryl Olefins in Nonprotic Media¹

Frank Scully, Tom Nylund, Fred Palensky, and Harry Morrison*

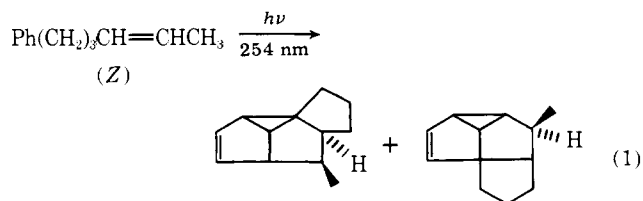
Contribution from the Department of Chemistry, Purdue University,
West Lafayette, Indiana 47907. Received April 25, 1978

Abstract: Three nonconjugated aryl olefins, having well-defined but varied interorbital angles between the chromophores, have been studied: 2-methylenebenzborbornene (MBN), 2-ethylidene-1-methylindan (EMI), and 1-ethylidene-8,9-benzospiro[3.5]nonane (ESO). The latter two are new compounds and their syntheses are detailed. In all cases, photoelectron, ultraviolet absorption, and fluorescence emission spectra have been measured. The solution-phase photochemistry of these molecules, using 254-nm irradiation, has been elaborated; MBN reacts primarily via a "diverted di- π -methane" reaction while EMI, ESO, and 2-isobutylidenebenzborbornene (IBN) undergo a facile olefin *E/Z* photoisomerization. Xenon perturbation methods have been used to gain insight into the relative involvement of singlet and triplet states in these reactions, and it appears that both states participate. Singlet interaction between the chromophores is a function of their geometry, being greatest in MBN (where appreciable charge transfer occurs in polar media), reduced in EMI, and minimal in ESO. Interaction at the triplet level is complete in all cases, there being no aryl phosphorescence observed for any of the substrates. An important feature of both MBN and EMI is extensive nonradiative decay from the singlet and triplet states; this decay is caused by the presence of the olefin moieties, does not involve olefin isomerization, and may well be general for nonconjugated aryl olefins.

The systematic study of bi- and polychromophoric molecules has generated considerable interest,^{2,3} representing as it does the logical extension of the intensive surveys of monofunctional compounds which dominated photochemistry until recent years. Our own efforts in this area have proceeded at two levels: (a) we have been examining ground- and excited-state interactions between functionalities in conformationally mobile, acyclic systems² and (b) we have been studying these interactions in relatively rigid carbon frameworks. Each of the above has advantages with regard to obtainable information. Flexible systems provide a time-dependent spectrum of interchromophoric relationships which give rise to "preexcitation" and "postexcitation" interactions, and in fact may be used to obtain rate constants for bond rotations in chains.⁴ By contrast, rigid molecules permit one to study interactions as a function of well-defined interchromophoric distances and angular relationships.⁵

Among the functional group pairs examined in these laboratories, the aryl olefins have proven particularly fruitful, giving rise in acyclic arrays to both triplet and singlet interactions upon excitation of the benzene ring. Thus 6-phenyl-

2-hexene provided the first suggestion of, and evidence for, aryl olefin singlet exciplexes as precursors to cycloadducts.⁶ Following excitation, the two functionalities achieve a collinear arrangement (allowed for by the trimethylene "bridge"), which permits rapid ($4 \times 10^8 \text{ s}^{-1}$) complexation, almost complete fluorescence quenching, and eventual photochemistry (eq 1).



By contrast 1-phenyl-2-butene exhibits normal singlet photophysics but undergoes a facile, predominantly triplet derived, *E/Z* photoisomerization (eq 2).⁷

