Secondary Hydrogen Isotope Effect in the Unimolecular Decomposition of 2-Methylpropane Radical Cations

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Abstract: The intensities of the mass spectral metastable peaks for loss of methane from 2-methylpropane-*1,1,1,3,3,3-d*$_6$ reveal a strong secondary hydrogen isotope effect, in that the rate of loss of CH_3D is approximately an order of magnitude greater than the rate of loss of CD_3H, which in turn is several times greater than the rate of loss of CD_4. This isotope effect is interpreted in terms of a nonclassical transition state involving a three-center bond. This nonclassical structure is analogous to the transition state containing a three-center two-electron bond, believed to be involved in the reaction of 2-methylpropane with superacids. Photoionization appearance energies, determined for the molecular and fragment ions from 2-methylpropane, 2-methylpropane-*2-d*$_1$, and 2-methylpropane-*1,1,1,3,3,3-d*$_6$, and detailed rate calculations provide support for the nonclassical structure.

The organic chemistry of gaseous alkane radical cations has a superficial simplicity,[1] which in the past has made these systems popular choices for detailed theoretical study. Indeed, some of the most convincing evidence supporting absolute reaction rate theory, as applied to mass spectrometry, concerns alkane ions.[2] One of the major reactions of alkane ions is the rearrangement effecting loss of methane, which has invariably been regarded as a concerted 1,2 elimination. In this paper, an intramolecular secondary hydrogen isotope effect of greater than 20 for loss of methane from the metastable 2-methylpropane ion is reported. This secondary isotope effect swamps the primary hydrogen isotope effect for the intramolecular hydrogen transfer involved in the reaction. Metastable ions are studied, because they have low internal energies and because the reactant and product ion masses of any particular decomposition are unambiguously defined. The nature of these isotope effects firmly excludes the concerted 1,2 elimination mechanism, and strongly suggests involvement of a nonclassical transition state analogous to transition states in carbonium ion chemistry.

The extensive literature on gaseous alkane ions tends to suggest that they resemble their neutral precursors in terms of structure.[1,3,4] The field ionization kinetics of deuterium-labeled 2-methylpropanes are consistent with decompositions of molecular ions, whose structures are qualitatively the same as those of their neutral precursors and in which atoms retain their original positional identities.[5] Isomerization of butane ions to the more stable 2-methylpropane ions has been discussed but the reverse has never been seriously proposed.[6] Although electron impact mass spectra of deuterium-labeled 2-methylpropanes and butanes show signs of small degrees of "hydrogen randomization", metastable peaks for the same compounds do not evidence any such nonspecific exchanges.[7-10] Similarly photoelectron-photoion coincidence measurements[8] find that the labeled propane $CH_3CD_2CH_3$ loses not only CH_4 but also CH_3D and CH_2D_2, whereas only one major metastable peak $(M)^{+\cdot} \rightarrow (M - CH_4)^{+\cdot}$ is observed for methane loss following electron impact.[4] Clearly, the internal energy required for nonspecific hydrogen arrangements is greater than that of metastable ions.

Experimental Section

Metastable peak intensities and shapes were measured using a new grand-scale mass spectrometer, which has been constructed in the Department.[11] This instrument employs a magnetic sector with a radius of 78 cm; the field-free region between source and magnet is 112 cm in length. A 0.25-mm wide source slit and a 0.40-mm wide collector slit were used for the measurements. These slit widths correspond to a mass resolution of approximately 2000. The pressure in the field-free region was of the order of 10^{-8} Torr (10^{-6} Pa).

Appearance energies have been measured using a photoionization mass spectrometer, which has been described in detail elsewhere.[12] It consists of a windowless hydrogen discharge lamp and a 1-m Seya-Namioka type monochromator (band-pass = 0.125 nm), together with a 15-cm-radius single-focusing magnet. A microcomputer is used for the on-line control of the instrument and for extended signal averaging of the experimental results.

Results

Metastable peak intensities for loss of methane from 2-methylpropane, 2-methylpropane-*2-d*$_1$, and 2-methylpropane-*1,1,1,3,3,3-d*$_6$ following electron impact are given in Table I. These intensities are expressed relative to the relevant molecular ion intensity. The relative intensities of metastable peaks for loss of methane from 2-methyl-*d*$_3$-propane-*2-d*$_1$ reported by Wolkoff and Holmes[4] are included in the table. No metastable peaks for loss of methyl radical were observed in our experiments. This means that the intensity of the metastable peak for loss of methyl radical from the 2-methylpropane molecular ion is less than 0.01 that of the metastable peak for loss of methane. That we do not observe this metastable peak for methyl loss, which has been reported by other workers,[4] may be a consequence of the low pressure (order of 10^{-8} Torr) in the field-free region of our instrument.

The photoionization efficiency curves for the molecular ions of 2-methylpropane, 2-methylpropane-*2-d*$_1$, and 2-methylpropane-*1,1,1,3,3,3-d*$_6$ are shown in Figure 1. The threshold for the 2-methylpropane curve is below 10.5 eV, and could be as low as 10.3 eV.[13] The ionization efficiency curves for the fragment ions formed by loss of methyl radical from the various 2-methylpropanes are shown in Figure 2. The curves for $(M - CH_3)^+$ from 2-methylpropane, $(M - CH_3)^+$ from 2-methylpropane-*2-d*$_1$, and $(M - CH_3)^+$ from 2-methylpropane-*1,1,1,3,3,3-d*$_6$ are identical. Linear extrapolation gives appearance energies of 11.16 eV (Table II).[14] The curve for $(M - CD_3)^+$ from the d_6 compound is very similar to the other three, differing only in that the tail of the curve is fuller.

Figures 3 and 4 show the ionization efficiency curves for the ions due to loss of methane from the various 2-methylpropanes. The curves for loss of CH_4 from the unlabeled compound (Figure 3a), loss of CH_4 from the d_1-labeled compound (Figure 3b), and loss of CH_3D from the d_6-labeled compound (Figure 4c) are virtually identical. The other two curves (Figures 4a and 4b—loss of CD_4 and CD_3H, respectively, from the d_6 compound) are similar to each other, but differ from these three (Figures 3a,b and 4c), notably in that they are shifted to higher energies (by about 80 meV at threshold). The

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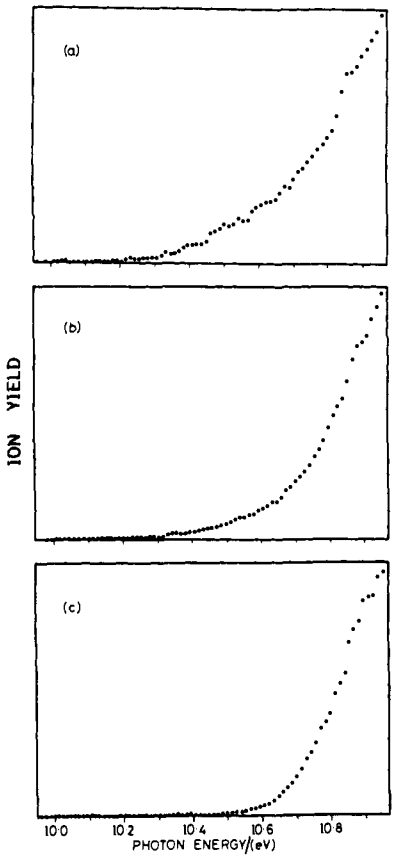


Figure 1. The photoionization efficiency curves for the molecular ions of (a) 2-methylpropane, (b) 2-methylpropane-*2*-d_1, and (c) 2-methylpropane-*1,1,1,3,3,3*-d_6.

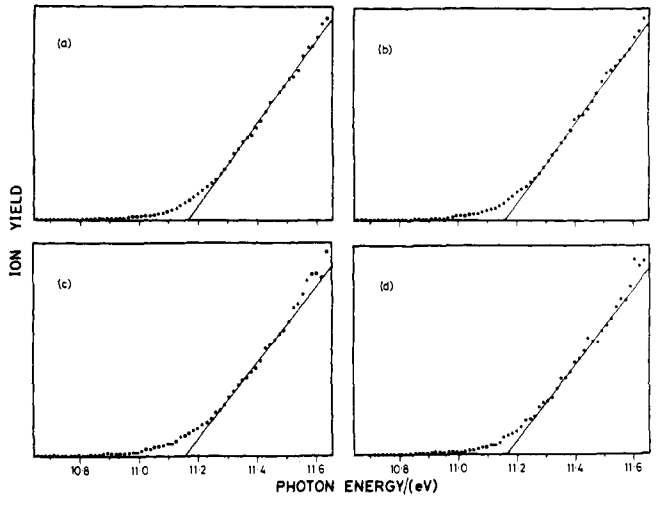


Figure 2. The photoionization efficiency curves for fragment ions formed by loss of methyl radical: (a) loss of CH_3· from 2-methylpropane; (b) loss of CH_3· from 2-methylpropane-*2*-d_1; (c) loss of CD_3· from 2-methylpropane-*1,1,1,3,3,3*-d_6; (d) loss of CH_3· from 2-methylpropane-*1,1,1,3,3,3*-d_6.

thresholds (Table II) for the curves in Figures 3 and 4 have again been obtained by the method of linear extrapolation. In every case, however, the amount of signal below the given threshold is more than can be attributed to thermal effects ("hot bands") and, therefore, these thresholds for methane loss (Table II) should be regarded as upper limits.

Discussion

The metastable peak intensities are the compelling results, as regards the mechanistic proposals advanced. The photo-

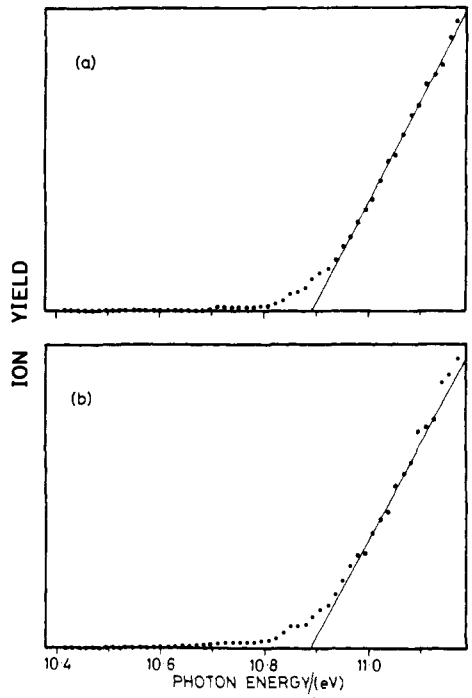


Figure 3. The photoionization efficiency curves for fragment ions formed by loss of methane: (a) loss of CH_4 from 2-methylpropane; (b) loss of CH_4 from 2-methylpropane-*2*-d_1.

Table I. Intensities of Metastable Peaks for 2-Methylpropanes Following Electron Impact

compd	intensity
$(CH_3)_3CH$[a]	$(M - CH_4)$ $6.0 \pm 0.5 \times 10^{-4}$
$(CD_3)_2CH_3CH$[a]	$(M - CH_3D)$ $3.4 \pm 0.1 \times 10^{-3}$ $(M - CD_3H)$ $4.0 \pm 0.8 \times 10^{-4}$ $(M - CD_4)$ $1.6 \pm 0.8 \times 10^{-4}$
$(CH_3)_3CD$	only $(M - CH_4)$ (no $(M - CH_3D)$)
$CD_3(CH_3)_2CD$[b]	$(M - CH_4)$ 0.78 ± 0.04 $(M - CH_3D)$ 0.18 ± 0.04 $(M - CD_3H)$ 0.01 ± 0.01 $(M - CD_2H_2)$ 0.02 ± 0.02

[a] These intensities are expressed relative to those of the molecular ion peaks. [b] Relative intensities from ref 4.

ionization appearance energies must, however, be discussed first in order to establish the structures of the reactant and product ions. This need to first address the question of the structures of these ions arises because it has recently been proposed[4] that the product ion has the cyclopropane structure (rather than the propene structure as indicated by our results).

The appearance energy of 10.89 eV for loss of methane from 2-methylpropane (Table II) is consistent with formation of the propene ion: 10.89 eV implies that the heat of formation of the transition state leading to $(C_3H_6)^{+\cdot}$ and CH_4 is 916 kJ mol^{-1}, which is 31 kJ mol^{-1} greater than the combined heats of formation of the propene ion and CH_4 (885 kJ mol^{-1}).[13] Wolkoff and Holmes[4] have proposed that it is the cyclopropane ion which is formed when methane is lost from 2-methylpropane, on the grounds that the small translational energy release (44 meV as measured in this work) indicates that the reaction has no reverse activation energy. There is, however, no a priori reason why most of the reverse activation energy of 31 kJ mol^{-1} (supposing formation of the propene ion) could not be partitioned as vibration and rotation rather than translation.[15]

Table II. Photoionization Appearance Energies (eV) of Fragment Ions of 2-Methylpropanes

compd	loss of methane	loss of methyl	loss of hydrogen atom
$(CH_3)_3CH$	$(M - CH_4)$ 10.89 ± 0.02 (10.91)[b] (10.93)[a]	$(M - CH_3)$ 11.16 ± 0.02 (11.23)[a] (11.23)[a]	$(M - H)$ 10.68 ± 0.02[c] (11.45)[b]
$(CD_3)_2CH_3CH$	$(M - CH_3D)$ 10.89 ± 0.02 $(M - CD_3H)$ 10.97 ± 0.02 $(M - CD_4)$ 10.97 ± 0.02	$(M - CH_3)$ 11.16 ± 0.02 $(M - CD_3)$ 11.16 ± 0.02	
$(CH_3)_3CD$	$(M - CH_4)$ 10.89 ± 0.02	$(M - CH_3)$ 11.16 ± 0.02	

[a] Reference 3. [b] Reference 4. [c] Reference 19.

The appearance energy of 10.89 eV, in fact, represents less energy than is required for formation of the cyclopropane ion and CH_4.[16]

The reactive molecular ion is considered to have a 2-methylpropane structure.[17] The appearance energy of 11.16 eV for loss of methyl radical from 2-methylpropane is consistent with formation of the 2-propyl ion[18] and the appearance energy of 10.68 eV for loss of a hydrogen atom is consistent with formation of the 2-methyl-2-propyl ion.[19] Both these ions can be formed from the 2-methylpropane ion by direct bond cleavages, in accord with the fact that "kinetic shift" does not appear to be a significant factor in these appearance-energy measurements.

The metastable peak intensities (Table I) show that the hydrogen atom on the tertiary carbon is not directly involved in the loss of methane from the 2-methylpropane ion. $(CD_3)_2CH_3CH$ shows no metastable peak for loss of CH_4, and $(CH_3)_3CD$ shows no peak for loss of CH_3D. In terms of the atoms involved, therefore, this reaction effecting loss of methane can be exactly described. A 2-methylpropane ion reacts to form a propene ion and methane, with the methane being made up of one of the original methyl groups plus a hydrogen atom from one of the other methyl groups.

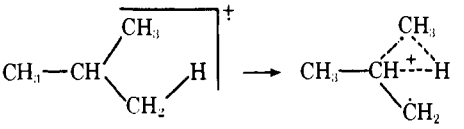
The relative intensities of the metastable peaks are proportional to the relative rates of the different decompositions, so it is evident that there are strong kinetic isotope effects for the loss of methane. The rate of loss of CH_3D from $((CD_3)_2CH_3CH)^{+\cdot}$ is over 20 times greater than the rate of loss of CD_4, although both reactions involve a D transfer. The rate of loss of CD_3H, involving an H transfer, is eight times less than the rate of loss of CH_3D, involving a D transfer. There is, therefore, a secondary hydrogen isotope effect of greater than 20, which outweighs the primary isotope effect on the H (or D) transfer.

It should be borne in mind that these isotope effects allow for little flexibility in their mechanistic interpretation, because they refer to competing reactions of the same reactant (i.e., they are *intramolecular* kinetic isotope effects). The competing reactions occur over the same potential-energy surface (within the Born-Oppenheimer approximation), and with the same internal energy. The isotope effects, therefore, provide definite information on the changes in vibrational frequencies on forming the reaction transition state. Moreover, the relative changes in frequencies for the different reactions (loss of CH_3D, CD_3H, and CD_4) must conform to the Teller-Redlich product rule. Further, these frequency changes determine precisely the differences in activation energies among the reactions (being the differences in zero-point energies).

That methane containing an original CH_3 group is lost in preference to one containing an original CD_3 group indicates that, on forming the transition states, frequencies of the C-X modes (X = H or D) of the methyl to be eliminated *fall* substantially.[20] These changes, through their effects on zero-point energies, result in the activation energy for loss involving CH_3 being less than that for a loss involving a CD_3 group. Hence, CH_3D is eliminated in preference to CD_3H (see calculations below). A fall in vibrational frequencies of these C-H (or C-D) modes indicates that these bonds weaken significantly on forming the transition states. This is particularly remarkable, given that the overall effect of the reaction is to convert this group to methane.

Given this significant weakening of C-H (C-D) bonds, we conclude that the methyl group to be eliminated has little methane character in the transition state. It would be unreasonable to suppose that the two products were already moving apart from each other, with C-H (C-D) bonding in the incipient methane weaker than in the reactant ion. Further, from the fact that the primary isotope effect on the hydrogen transfer is insignificant in comparison to the secondary isotope effect, we conclude that the hydrogen transfer is not rate determining. Expressed differently this means that in the transition state the carbon to be eliminated is still firmly bound to the rest of the molecule, while the hydrogen transfer is already complete.

To account for these conclusions, we propose the mechanism shown in eq 1. It is envisaged that a hydrogen on a methyl



$$\longrightarrow CH_3CH{=}\overline{CH_2}^{+} + CH_4 \quad (1)$$

group interacts with the electron density in a neighboring C-C bond. As the original C-H bond breaks, a three-center bond forms. This electron-deficient three-center bond draws electron density from the C-H bonds of the methyl group involved, thereby accounting for the weakening of these bonds. It is a moot point whether or not the structure containing the three-center bond is an intermediate; the kinetic isotope effect concerns the transition state in the rate-determining steps. The structure containing the three-center bond dissociates to form methane and the propene ion. The overall reaction to lose methane can, therefore, be regarded as an intramolecular substitution proceeding with retention of configuration.

It could be argued that a transition state of the type $CH_3(\dot{C}H_2)CHC^+H_4$, in which the transferred hydrogen interacts with only one carbon atom, would also account for the isotope effects. There are, however, two points weighing against this mechanism. Ab initio molecular orbital calculations[21] indicate that with $(C_2H_7)^+$, a structure in which the seventh hydrogen bridges between the carbon atoms, is significantly more stable than those in which this hydrogen is associated with just one carbon.[22] The second point is that $CH_3(\dot{C}H_2)$-CHC^+H_4 is not the most stable structure of its type. The structure $(CH_3)_2\dot{C}C^+H_4$ would be more stable than the primary radical $CH_3(\dot{C}H_2)CHC^+H_4$, and, if it were to exist, would provide a pathway for hydrogen randomization.[23] There is no evidence for hydrogen randomization within the 2-methylpropane ion at low energies.

The photoionization appearance energies (Table II) for loss of either CD_3H or CD_4 from the d_6 compound are higher than

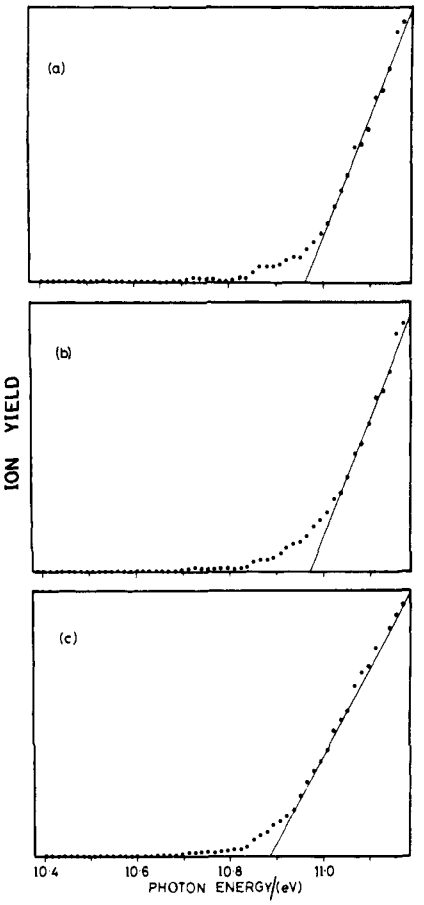


Figure 4. The photoionization efficiency curves for fragment ions formed by loss of methane from 2-methylpropane-*1,1,1,3,3,3-d*$_6$: (a) loss of CD_4; (b) loss of CD_3H; (c) loss of CH_3D.

that for loss of CH_3D (by 80 meV or 8 kJ mol^{-1} at threshold). As mentioned before, these three reactions occur over the same potential-energy surface, and therefore differences in appearance energies reflect the effects of changes in vibrational frequencies on moving to the transition state. It follows that the C-H (C-D) bonds in the methyl group to be eliminated as methane must be significantly weaker in the transition state, as compared to the reactant. The appearance energies therefore provide strong support for the conclusions drawn from the kinetic isotope effects.

The proposed rearrangement (1) is an intramolecular analogy of the ion-molecule reaction of methane, in which the molecular ion reacts with the neutral molecule to form a methyl radical and the carbonium ion $(CH_5)^+$ (ref 24). This reaction is either exoergic or energetically neutral.[25] The carbonium ion $(C_2H_7)^+$ has also been observed by mass spectrometry.[24,26,27] The ion $(C_4H_{11})^+$ has not actually been observed in studies of ion-molecule reactions of 2-methylpropane.[24,26,28] It is, however, believed that proton transfer to 2-methylpropane does occur readily,[26] but that the $(C_4H_{11})^+$ ions so formed are unstable and decompose to give either $(C_3H_7)^+$ by loss of methane or $(C_4H_9)^+$ by loss of hydrogen.[28]

To investigate whether the sorts of changes in vibrational frequencies predicted by the mechanism (eq 1) are of the right magnitude to account for the differences in appearance energies, and whether in turn those differences in appearance energies are sufficient to account for the observed isotope effects, rates of decomposition have been calculated on the basis of quasi-equilibrium theory.[29] The expression (2) has been evaluated by counting states.[30]

$$k(E) = \frac{\sigma G^*(E - E_0)}{hN(E)} \qquad (2)$$

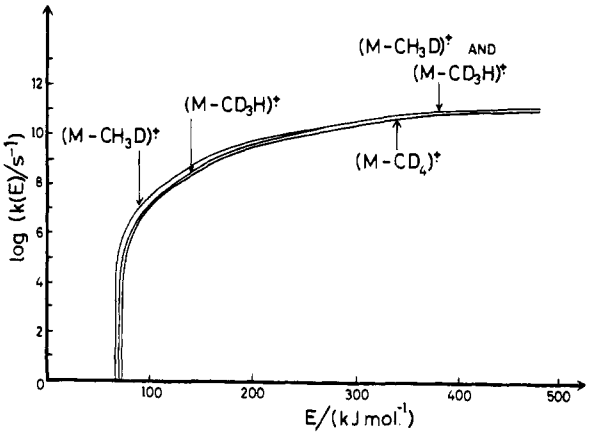


Figure 5. The calculated rate constants $k(E)$ as a function of internal energy E for the loss of CH_3D, CD_3H, and CD_4 from the $(CD_3)_2CH_3CH$ radical cation.

E_0 is the activation energy of the reaction, $G^*(E - E_0)$ is the total number of states of the activated complex within the energy interval $(E - E_0)$, $N(E)$ is the density of states at energy E for the reactant ion, h is Planck's constant, and σ is the number of equivalent paths for the reaction. The vibrational frequencies used for the 2-methylpropane ion are those of the neutral and are listed in the Appendix. The calculations yield rate constants $k(E)$ as a function of the internal energy E for an individual decomposition. The metastable peak intensity depends upon the rate constant $k(t)$, which represents the rate of decomposition at time t for a given assembly of molecular ions. $k(E)$ and $k(t)$ are related through the expression 3 (ref 31). $P(E)$ is the internal energy distribution of the 2-methylpropane ion.

$$k_1(t) = \int_{E_0}^{E} P(E)k_1(E)e^{-(k_1(E)+k_2(E)+k_3(E))t}\,dE \qquad (3)$$

The expression 3 refers to a situation in which three reactions (distinguished by the subscripts 1, 2, and 3) are competing with each other. The rate constants $k(t)$ presented below have been obtained from the calculated $k(E)$ by means of expression 3, assuming that $P(E)$ is uniform throughout the energy range of interest.

Considering the d_6 compound, the vibrational frequencies of the molecular ion have been obtained by adjusting those of the unlabeled compound in accord with the Teller-Redlich product rule.[30] The changes which have been made for the transition states, as compared to the molecular ion, have been to lower each of the C-X (X = H or D) stretches and bends of the methyl group to be lost as methane by 20%. The stretching and bending frequencies of the transferred hydrogen (H or D, as the case may be) have been lowered marginally (~10%). These adjustments, through their effects on zero-point energies, make the activation energy for loss of CD_4 higher than that for loss of CD_3H by 50 cm^{-1} (~0.6 kJ mol^{-1}), which in turn is higher than that for loss of CH_3D by 350 cm^{-1} (~4 kJ mol^{-1}). The reaction coordinate has been taken as a C-CX_3 bend. Removing this frequency affects the zero-point energy also, making the activation energies for loss of CH_3D or CD_4 higher than that for CD_3H by about 50 cm^{-1}. Summing these two contributions leads to the conclusion that the activation energy for loss of CH_3D is less than that for loss of CD_3H by 4 kJ mol^{-1} (300 cm^{-1}), which in turn is less than that for loss of CD_4 by 1 kJ mol^{-1} (100 cm^{-1}). The actual values of the activation energies which have been used are 67, 71, and 72 kJ mol^{-1}. The symmetry factor σ has been taken as 6 for each of the three reactions.

The $k(E)$ vs. E curves for loss of the variously labeled methanes from the d_6 compound are shown in Figure 5. The

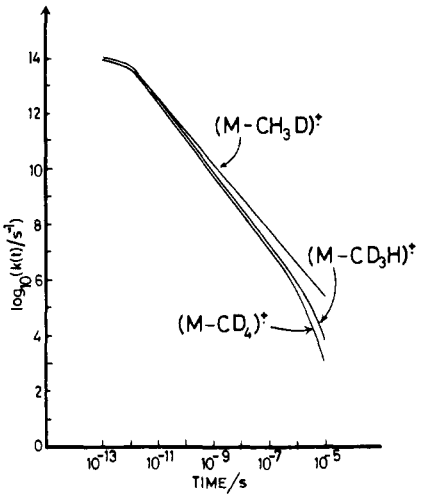


Figure 6. The rates $k(t)$ as a function of reaction time (i.e., ion lifetime) for the loss of CH_3D, CD_3H, and CD_4 from the $(CD_3)_2CH_3CH$ radical cation.

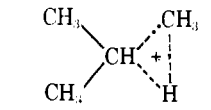
$k(t)$ vs. t curves for the same decomposition are shown in Figure 6. It is the *relative* values of $k(t)$ for the various decompositions at any particular time t which are significant (the absolute values depend on the normalization of $P(E)$). To obtain a measure of the metastable peak intensity, the $k(t)$ function must be integrated over the time window corresponding to metastable ions. In the large mass spectrometer employed for the measurements, this window is 8 μs for an ion of m/z 64 at an accelerating voltage of 10 kV. If it is supposed that the molecular ions take $\sim$1 μs to escape from the electron impact source, it is the values of $k(t)$ between 1×10^{-6} and 9×10^{-6} s, which determine the abundances of metastable ions. We have taken the relative intensities of the metastable peaks as a measure of the relative abundances of the metastable ions. The area under the $k(t)$ vs. t curves for loss of CH_3D, CD_3H, and CD_4 over the range 1×10^{-6} to 9×10^{-6} s are in the ratio 25:3:1. These compare to the corresponding ratios for the metastable peak intensities, 21:3:1 (Table I).

Calculations have also been performed for the loss of methane from $CD_3(CH_3)_2CD$, using the same model as for the d_6 compound. The ratios of the areas under the $k(t)$ curves in this case are 70:30:1 for loss of CH_4, CH_3D, and CD_3H, respectively. These compare with the ratios 78:18:1 for the metastable peak intensities[4] (Table I).

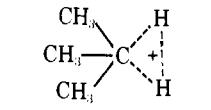
Conclusion

According to the proposed mechanism (eq 1), the loss of methane from the 2-methylpropane radical cation is initiated by transfer of a hydrogen atom of a methyl group to interact with the electron density in a C-C bond. According to this view, the loss of methane is an intramolecular substitution reaction. The hydrogen inserts into the C-C bond and the C-C bond is replaced by the C-H bond. The significance of the three-center bond would be that it facilitates the approach of the attacking group on that same side of the methyl from which the departing group must leave.

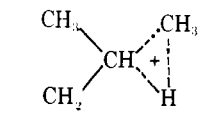
The proposed mechanism has relevance for carbonium ion chemistry. Olah et al.[32] proposed some years ago that in superacid protolytic attack on alkanes occurs at the C-H or C-C bonds, rather than on the hydrogen or carbon atoms themselves. With 2-methylpropane, it is proposed[32] that protiolysis at the tertiary C-H bond is preferred over protiolysis at a C-C bond. The former leads to loss of H_2 and the latter to loss of CH_4. The transition-state structure proposed here (eq 1) is closely analogous to the proposed transition state in protiolysis of a C-C bond in superacid. Both involve three-center two-electron bonds, and both decompose to lose methane. The



superacid—loses CH_4



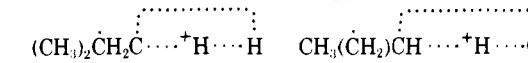
superacid—loses H_2



gas phase—loses CH_4

gas-phase mechanism, which rests on the evidence of intramolecular kinetic isotope effects, lends support, therefore, to the C-C protiolysis mechanism proposed for the solution reaction.

The proposal for the solution reaction is that the structure formed by protiolysis of a tertiary C-H has a lower energy than that formed by protiolysis of a C-C bond, which in turn has a lower energy than the structure from protiolysis of a primary C-H.[32] According to this view, therefore, the gas-phase structure i would have a lower energy than ii. There is, however,



i ii

no evidence to support the existence of the former structure,[33] and we conclude that in the gas phase the three-center two-electron bond involving two hydrogen atoms and one carbon atom is significantly higher in energy than the three-center bond involving two carbons and one hydrogen.[34]

Appendix I. Synthesis

The samples of $(CH_3)_3CH$, $(CH_3)_3CD$, and $(CD_3)_2CH_3CH$ were synthesized by the same general method.

In the case of $(CD_3)_2CH_3CH$, the starting materials were methyl iodide and acetone-*1,1,1,3,3,3-d*$_6$. These compounds were reacted with magnesium in ether at 0 °C to form the Grignard compound $(CD_3)_2CH_3CMgI$, which was decomposed to the 2-methylpropan-2-ol by addition of dilute hydrochloric acid.[35] The alcohol was separated by distillation and converted to 2-methyl-2-chloropropane by treatment with concentrated hydrochloric acid and anhydrous calcium chloride. The chloride was distilled and refluxed with ether, magnesium, and a small amount of iodine to form the Grignard compound $(CD_3)_2CH_3CMgCl$. Dilute hydrochloric acid was added to the Grignard compound at 0 °C, and the evolved gases were condensed and collected. It was found that approximately equal yields of 2-methylpropane and 2-methylpropene were obtained. The alkene was removed by converting it to 2-methyl-1,2-dibromopropane. The 2-methylpropane was distilled several times and stored under liquid nitrogen.

The unlabeled 2-methylpropane was synthesized in the same fashion, except that the starting material was the unlabeled acetone $(CH_3)_2CO$. For $(CH_3)_3CD$, D_2O was used instead of H_2O in the final step.

The isotopic purities of the samples were determined by photoionization mass spectrometry (ionizing energies in the range 8-14 eV) and checked by low-energy electron impact mass spectrometry. The only impurity in the d_6 samples was $CD_3(CD_2H)(CH_3)CH$, which was present to the extent of no more than a few percent. The d_1 sample contained a few percent of the unlabeled compound. It was found to be unnecessary to correct any of the measurements for the presence of these isotopic impurities.

Appendix II. Vibrational Frequencies

The vibrational frequencies of the neutral 2-methylpropane[36] were used in the calculations to represent the

frequencies of the unlabeled 2-methylpropane ion. These frequencies (cm^{-1}) were 2964, 2964, 2963, 2960, 2960, 2959, 2904, 2882, 2882, 2882, 1466, 1466, 1463, 1459, 1458, 1458, 1375, 1370, 1370, 1314, 1314, 1181, 1181, 1168, 981, 955, 955, 904, 904, 791, 418, 381, 381, 203, 203, 198.

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(18) 11.16 eV leads to a heat of formation of 800 kJ mol^{-1} for $(C_3H_7)^+$, neglecting any excess energy terms and using $\Delta H_f°_{298}$(2-methylpropane) = −134.5 kJ mol^{-1} and $\Delta H_f°_{298}(CH_3\cdot$ = 142.3 kJ mol^{-1}. Thermodynamic data is according to H. M. Rosenstock et al. (ref 13). The value of 800 kJ mol^{-1} compares with the figures of 784 kJ mol^{-1} obtained by F. A. Houle and J. L. Beauchamp (*J. Am. Chem. Soc.*, **101**, 4067 (1979)) and 787 kJ mol^{-1} obtained by J. C. Traeger (*Int. J. Mass Spectrom. Ion Phys.*, **32**, 309 (1980)) for the heat of formation of the 2-propyl ion.
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