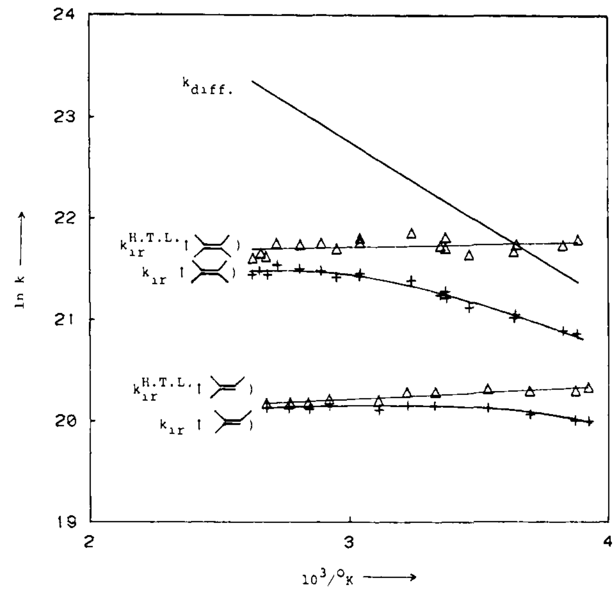

Figure 4. The Arrhenius behavior of k_{ir} and k_{ir}^{HTL}, for tetramethylethylene and trimethylethylene, and k_{diff}.

substituted olefins, having lower IP's, have more negative values of $\Delta H°_{ex}$. These molecules also have correspondingly larger values of $E_{a,2}$. Consequently steric effects play an important role in decreasing the rate of biradical formation and make the apparent sensitivity of k_{ir} to quencher ionization potential less than that one might observe if one could measure $\Delta H°_{ex}$ and the equilibrium constant for exciplex formation.

Second, virtually all *gas-phase* additions of multiatom radicals to alkenes show A factors of ca. 1×10^8 s^{-1}. If exciplex decay to biradical is rate determining, its A factor should be similar; the entropy of biradical formation from the separated reactants is independent of whether an exciplex intermediate precedes the reaction transition state. Third, correlations of log k_{ir} vs. IP must be interpreted with care. Our data indicate that the slopes of such plots are temperature dependent and that steric effects operate to oppose the dependence of $\Delta H°_{ex}$ upon quencher ionization potential.

Summary

An Arrhenius study has been carried out for quenching of phosphorescence in carbon tetrachloride of a substituted benzophenone, 4-carboxymethylbenzophenone, by a series of simple alkenes. The Arrhenius plots are characterized by very low activation energies (0 to 1.8 kcal/mol), and, for the less reactive alkenes, A factors typical for the addition of radicals to carbon–carbon double bonds.

A new criterion has been established for identifying a nonemissive exciplex, namely a curved Arrhenius plot in an emission quenching reaction, signifying a change in the rate-limiting step with a change in temperature. This change was associated with a transition from diffusion-controlled exciplex formation at low temperatures to reversible exciplex formation followed by rate-determining exciplex deactivation at high temperatures.

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Unimolecular Reactions of Ionized Alkanes

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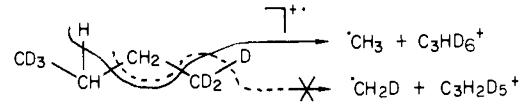
Abstract: The unimolecular reactions of several $C_nH_{2n+2}^{+\cdot}$ radical cations are discussed in terms of species involving an incipient carbonium ion coordinated to a radical. These species can be formed by stretching the appropriate bond in the ionized alkane. Subsequent isomerization of the incipient carbonium ion can give rise to rearranged structures in which a 1,2-alkyl shift has effectively occurred. By means of such mechanisms, much of the previously reported data concerning decomposition of ionized *n*-butane can be explained; in particular, the results of ^{2}H-labeling studies can be interpreted. In addition, new labeling data are reported for ionized *n*-pentane and isopentane; the results indicate that both 1,2-methyl and 1,2-ethyl shifts precede or accompany dissociation of these $C_5H_{12}^{+\cdot}$ species. Previously published ^{13}C- and ^{2}H-labeling data on ionized *n*-heptane are also considered; these results can be understood in terms of competing 1,2-methyl, -ethyl, and -propyl shifts.

Introduction

The unimolecular reactions of ionized alkanes have been the subject of extensive research.[2-17] Although the chemistry of alkanes is generally regarded as being simple, because of the absence of functional groups, this is certainly not true for the ionized compounds. Extremely complex behavior is frequently observed, even for relatively small $C_nH_{2n+2}^{+\cdot}$ species; loss of alkyl

Scheme I



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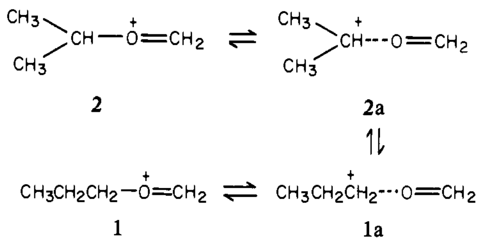
Scheme II



radicals and alkane molecules, often in competition, are common decomposition channels for the molecular ions of saturated hydrocarbons. For example, the molecular ion of *n*-heptane undergoes several reactions, including elimination of a methyl radical; there is a finite possibility of losing the carbon atom of the methyl radical from any position within the original carbon chain. The relative probabilities of losing a carbon atom from the 1, 2, 3, and 4 positions are respectively 26, 3, 18, and 6 at 70 eV and 30, 0, 18, and 17 at 11.5 eV.[14] Such data illustrate the complexity of reactions undergone by ionized alkanes; further examples can be found in ^2H-labeling studies on other systems.

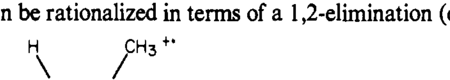
A variety of rationalizations have been offered to explain the dissociations of these ions, including simple cleavage of C–C bonds (before or after isomerization), processes involving extrusion of methylene groups from the original chain,[15,16] "flexures",[9] and cyclic transition states. These "flexures" and extrusion processes are without mechanistic precedent in organic chemistry. Indeed, the observed reactions have often appeared so bizarre that the question of mechanism has had to be circumvented almost completely. For example, the rationalization[15] of $\dot{C}H_3$ loss from $CD_3CH_2CH_2CD_3^{+\cdot}$, and the absence of $\dot{C}H_2D$ loss, as an extrusion process is shown in Scheme I.

In these processes, conventional aspects of mechanistic organic chemistry are invoked only insofar as the occurrence of $\dot{C}H_3$ loss, and the absence of $\dot{C}H_2D$ loss, is justified in terms of a possible preference for selecting a hydrogen atom from a secondary, rather than a primary, site.[15]

Recent papers[15,16] summarize the evidence for and against the hypothesis that isomerization precedes decomposition of $C_nH_{2n+2}^{+\cdot}$ ions. What is now required is a theory which provides a unified basis for understanding possible rearrangements undergone by the carbon skeleton of ionized *n*-alkanes upon electron impact. It might reasonably be hoped that such a theory would rely only on previously established aspects of mechanistic organic chemistry. Indeed, rearrangement of alkyl side chains prior to dissociation has been inferred for oxonium ions.[18-21] For instance, a 1,2-hydride shift can lead to interconversion of **1** and **2**, via **1a** and **2a**, at lower energies than those needed to promote elimination of H_2O and CH_2O.[20] Such mechanisms (Scheme II) require the stretching of a given bond to a sufficient degree that a species resembling a carbonium ion is produced; rearrangement of this incipient carbonium ion (in this case $C_3H_7^+$) can then occur, prior to decomposition. The importance of Scheme II lies in the unification of concepts used in gas-phase ion chemistry and in solution chemistry. The isomerization of isolated normal to secondary carbonium ions (**1a** → **2a**) is well established in solution chemistry. In the case exemplified in Scheme II, the isomerization is reversible (**2a** ⇌ **1a**) since the ion/dipole binding in complex **2a** is greater than the energy (ca. 16 kcal mol^{-1}) required to convert the secondary carbonium ion of **2a** to the primary carbonium ion of **1a**.[20] In the present paper, we show that a model similar to that exemplified in Scheme II provides a unifying mechanism for some of the apparently surprising reactions undergone by ionized *n*-alkanes. In testing our hypothesis, we have studied *n*-pentane and isopentane, and utilized previously published data on *n*-butane and *n*-heptane.

Results and Discussion

Before presenting the data for $C_5H_{12}^{+\cdot}$, it is appropriate to review briefly the observed behavior of the lower homologue $C_4H_{10}^{+\cdot}$. Both $(CH_3)_3CH^{+\cdot}$ and $CH_3CH_2CH_2CH_3^{+\cdot}$ eliminate CH_4 in slow reactions, as evidenced by the presence of metastable peaks in the mass spectra of isobutane and *n*-butane. Collisional activation studies establish that the $C_3H_6^{+\cdot}$ ion, produced by CH_4 loss from ionized *n*-butane, has the structure $CH_3CH{=}CH_2^{+\cdot}$.[17] This can be rationalized in terms of a 1,2-elimination (eq 1), which


(1)

may, or may not, be concerted. However, this simple mechanism does not provide an adequate general explanation because $CD_3CH_2CH_2CD_3^{+\cdot}$ loses some CH_3D, and $CH_3CD_2CD_2CH_3^{+\cdot}$ eliminates some CD_3H in metastable transitions.[15] Two possible explanations may be advanced for this "internal" loss of methane: first, an extrusion process could operate resulting in loss of an original methylene group in the eliminated methane molecule;[16] second, isomerization of the ionized *n*-butane to ionized isobutane might precede dissociation. In the second case, we now postulate that rearrangement could occur via species involving incipient propyl cations (Scheme III) In this scheme, **3a**, **4a**, and **4b** represent species in which an originally covalent C–C bond has been effectively broken (see dashed lines). These loose complexes of carbonium ions and methyl radicals are, however, weakly bound relative to the completely separated carbonium ion and radical. For example, polarization of the electron cloud of the incipient radical gives rise to weakly bonding ion/induced dipole attractions in **3a**, **4a**, and **4b**. A closely analogous interaction in solution would be the solvation of a carbonium ion.

A number of facts relating to Scheme III, and experimental evidence which supports it, are now presented.

(i) The isomerization **3a** → **4a** must be rate determining en route to production of the isopropyl-d_3 cation with loss of a CD_3 radical. This follows since **4a** has been defined as being weakly bonded (a few kcal mol^{-1}) relative to these products; yet its production from **3a** ensures that its excess energy content will be $\sim$16 kcal mol^{-1}. Thus, dissociation (low E_a) of the energetically excited **4a** produced from **3a** will effectively preclude the reversion **4a** → **3a** ($E_a \simeq$ 16 kcal mol^{-1}).

Additionally, since the loss of deuterated methanes from **4** has a lower activation energy than methyl radical loss (by some 7 kcal mol^{-1} [23]), **3a** → **4a** will also be rate-determining and irreversible en route to loss of deuterated methanes from **3**.

(ii) As a consequence of the above conclusion (that **3a** → **4a** produces **4a** with a relatively high internal energy), loss of deuterated methanes from **4a** produced in this way will release more kinetic energy[22] than the corresponding losses commencing from **4**. This effect has indeed been observed; CH_4 eliminations from $CH_3CH_2CH_2CH_3^{+\cdot}$ and $(CH_3)_3CH^{+\cdot}$ are characterized by average kinetic energy releases of 1.5 and 1.0 kcal mol^{-1}, respectively.[15]

(iii) We require that, in metastable transitions, **3** decompose via a rate-determining rearrangement (**3a** → **4a**). Consequently, the energy barrers to losses of $\dot{C}H_3$ and CH_4 from ionized *n*-butane are determined by that for **3a** → **4a**; therefore, they should be the same within experimental error for both processes.[22] They do indeed differ by only 0–1 kcal mol^{-1}.[3,15,23]

(iv) Since CH_4 loss from ionized isobutane has a lower activation energy than $\dot{C}H_3$ loss (see above), the former process is dominant in metastable transitions.[23] Methane losses from the proposed intermediate (e.g., **4a**) will be subjected to a more stringent ordering in the transition state than will methyl radical losses (the former involving rearrangement). Consequently, the

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Scheme III

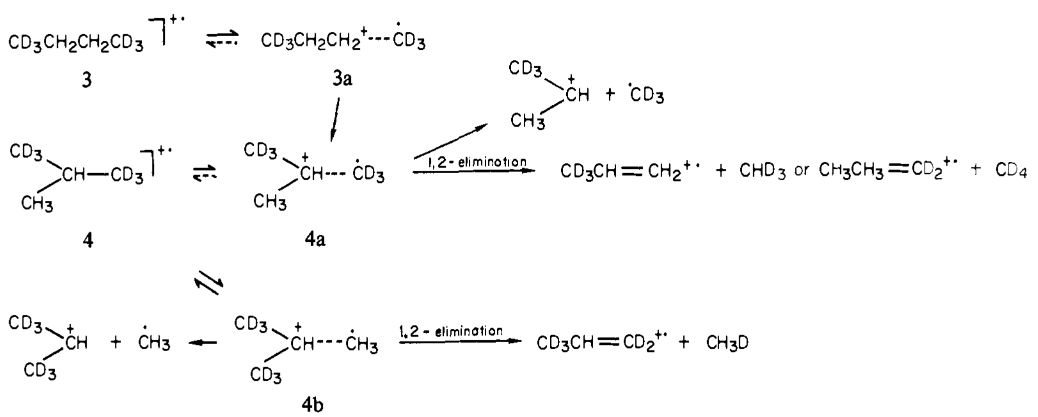


Table I. Unimolecular Reactions of Metastable $C_5H_{12}^{+\cdot}$ Ions

	neutral lost[a]			
ion	$\dot{C}H_3$	CH_4	$\dot{C}_2H_5$	C_2H_6
$CH_3CH_2CH_2CH_2CH_3^{+\cdot}$	13	16	1	70
$(CH_3)_2CHCH_2CH_3^{+\cdot}$		83		17

[a] Values measured by peak height and normalized to a total metastable ion current of 100 units (*B*/*E* scans).

rate constant for methane losses from **4a** will rise less rapidly with internal energy of **4a** than will methyl radical losses.[22] Therefore, when the undeuterated analog of **4a** is produced with a relatively high internal energy from ionized *n*-butane, CH_4 and $\dot{C}H_3$ are lost in approximately equal abundance in metastable transitions.

(v) Methyl radical loss from ionized *n*-butane has been investigated using ^2H-labeled analogs.[15] For example, $CD_3CH_3CH_2CD_3^{+\cdot}$ loses $\dot{C}D_3$ and a minor amount of $\dot{C}H_3$, but no $\dot{C}H_2D$. These observations can be readily interpreted using Scheme III: after the isomerization **3a** → **4a** has occurred, an ion is produced which contains two $-CD_3$ groups and one $-CH_3$ group, but no $-CH_2D$ group. When bond cleavage occurs in **4a** (or in closely related species such as **4b**), $\dot{C}D_3$ or $\dot{C}H_3$ can be lost, but no possibility exists whereby $\dot{C}H_2D$ or $\dot{C}D_2H$ can be lost. Consequently, the absence of $\dot{C}H_2D$ and $\dot{C}D_2H$ losses is explained. Moreover, the preference for $\dot{C}D_3$ elimination can also be understood on the assumption that **4a** dissociates more readily than it isomerizes to **4b** via **4**. In other words, there is a preference for eliminating the incipient radical involved in the isomerization process. Further evidence for this preference for eliminating the incipient methyl radical, which migrates during the rearrangement process, is furnished by ^{13}C-labeling results for homologous $C_nH_{2n+2}^{+\cdot}$ ions. The case of *n*-$C_7H_{16}^{+\cdot}$ is discussed in detail subsequently.

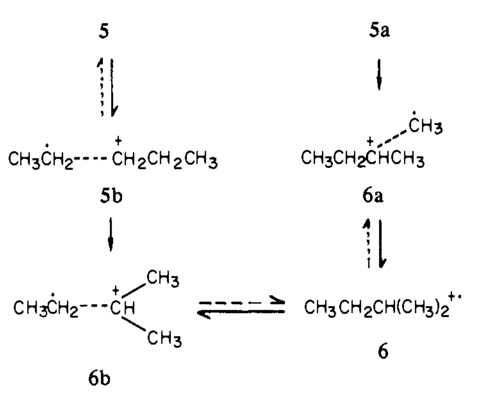
The observation[16] that methane losses from directly generated **4** comprise 91% loss of CH_3D is not inconsistent with the loss of only 5.6% of CH_3D from **3**. The former selectivity (91%) is presumably due to a secondary isotope effect. Since **3** → **3a** → **4a** produces **4a** (and possibly **4** and **4b**) with excess energy, any secondary isotope effect will be greatly reduced. Moreover, since the initially generated iso structure is **4a**, $CHD_3(CD_4)$ elimination may be enhanced.

The above analysis explains the behavior of isomeric $C_4H_{10}^{+\cdot}$ ions in terms of species involving an incipient carbonium coordinated to a radical. The theory is unifying and accounts for the available experimental facts. In the case of $C_5H_{12}^{+\cdot}$, more complex behavior is possible because ethyl radical migrations become feasible. This case is now discussed as a further test of the theory.

Ionized *n*-Pentane and Isopentane

The slow unimolecular reactions of $CH_3CH_2CH_2CH_2CH_3^{+\cdot}$ and $(CH_3)_2CHCH_2CH_3^{+\cdot}$ are given in Table I; these data show a marked similarity with those observed for $CH_3CH_2CH_2CH_3^{+\cdot}$ and $(CH_3)_2CHCH_3^{+\cdot}$: alkane losses are more dominant, compared to radical losses, when branched alkane molecular ions are involved. This suggests that ionized *n*-pentane isomerizes to ionized isopentane; there are two possible mechanisms for such an isomerization (Scheme IV).

Scheme IV



In the case of the mechanism involving the methyl radical shift, **5** → **5a** → **6a**, a rate-determining rearrangement (**5a** → **6a**) is supported by the greater average kinetic energy release associated with CH_4 loss from **5** (2.5 kcal mol^{-1}) compared to CH_4 elimination from **6** (2.1 kcal mol^{-1}).[15] A similar effect is observed for C_2H_6 loss from **5** and **6**; the average kinetic energies released upon elimination of C_2H_6 from **5** and **6** are 1.3 and 1.1 kcal mol^{-1}, respectively. These data, concerning elimination of CH_4 and C_2H_6 from **5** and **6**, suggest that some (or all) ions generated as **5** undergo rate-determining isomerization to **6** (or branched structures related to **6**), prior to alkane loss, from metastable ions. Such a postulate is supported by appearance energy measurements for CH_4 loss, which reveal that dissociation occurs via a transition state of lower energy (by 8–9 kcal mol^{-1}) starting from **6** than is the case beginning from **5**.[3,15,23] Moreover, essentially identical activation energies are needed to promote $\dot{C}H_3$ and CH_4 elimination from **5**; in contrast, $\dot{C}H_3$ loss from **6** is a very minor process requiring some 9 kcal mol^{-1} more energy than CH_4 elimination.[22] These energy measurements support the view that a rate-determining rearrangement is involved in the decomposition of **5** but not in dissociation of **6**.

Further insight into the chemistry of **5** and **6** is furnished by our ^2H-labeling results summarized in Tables II and III.

(a) ^2H-Labeled *n*-Pentanes (Table II). The slow reactions of ionized ^2H-labeled *n*-pentanes exhibit a greater complexity that those observed for the branched isomers. This arises because ionized *n*-pentane loses $\dot{C}H_3$ and CH_4 in comparable amounts, whereas ionized isopentane undergoes very little $\dot{C}H_3$ elimination. Nevertheless, a number of conclusions can be drawn from the results of Table II.

(i) Elimination of species such as $\dot{C}H_2D/CH_4$, $\dot{C}HD_2/CH_3D$, and, in particular, CH_2D_2 from $CH_3CH_2CD_2CH_2CH_3^{+\cdot}$ confirms that isomerization of ionized *n*-pentane must precede or accompany dissociation. These observations can be explained in terms of competing 1,2-methyl and 1,2-ethyl shifts (Scheme V). In view

Table II. Unimolecular Reactions of Metastable ^{2}H-Labeled Pentane Radical Cations

parent ion (*m*/*z*)	daughter ion, *m*/*z*	rel abundance[a]	neutral(s) lost
$CH_3CH_2CD_2CH_2CH_3^{+\cdot}$ (74)	59	8	$\dot{C}H_3$
	58	10	$\dot{C}H_2D/CH_4$
	57	4	$\dot{C}HD_2/CH_3D$
	56	8	CH_2D_2
	45	1	$\dot{C}_2H_5$
	44	45	$(\dot{C}_2H_4D)/C_2H_6$
	43	23	$(\dot{C}_2H_3D_2)/C_2H_5D$
	42	1	$C_2H_4D_2$
$CH_3CD_2CH_2CD_2CH_3^{+\cdot}$ (76)	61	10	$\dot{C}H_3$
	60	9	$\dot{C}H_2D/CH_4$
	59	7	$\dot{C}HD_2/CH_3D$
	58	4	$\dot{C}D_3/CH_2D_2$
	45	1	$\dot{C}_2H_3D_2/C_2H_5D$
	44	60	$(\dot{C}_2H_2D_3)/C_2H_4D_2$
	43	9	$(\dot{C}_2HD_4)/C_2H_3D_3$
$CH_3CH_2CH_2CH_2CD_3^{+\cdot}$ (75)	60	10	$\dot{C}H_3$
	59	12	$(\dot{C}H_2D)/CH_4$
	58	<0.5	$(\dot{C}HD_2)/CH_3D$
	57	2	$\dot{C}D_3/(CH_2D_2)$
	56	4	CHD_3
	46	0.5	$\dot{C}_2H_5$
	45	25	$(\dot{C}_2H_4D)/C_2H_6$
	44	15	$(\dot{C}_2H_3D_2)/C_2H_5D$
	43	0.5	$\dot{C}_2H_2D_3/C_2H_4D_2$
	42	31	$C_2H_3D_3$

[a] Values measured by peak height and normalized to a total metastable ion current of 100 units (*B*/*E* scans).

Table III. Unimolecular Reactions of Metastable ^{2}H-Labeled Isopentane Radical Cations

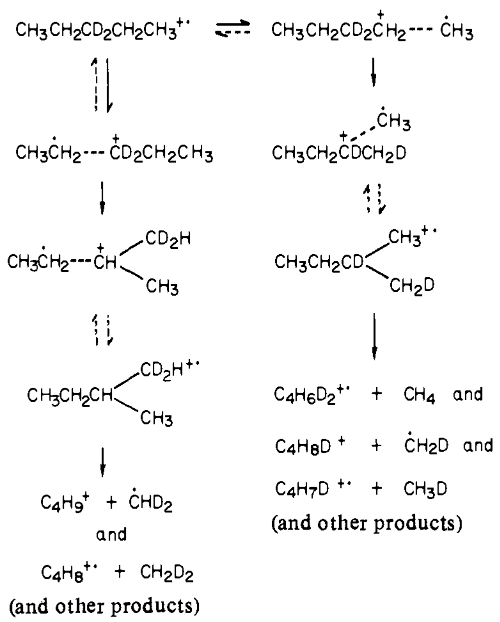
parent ion (*m*/*z*)	daughter ion, *m*/*z*	rel abundance[a]	neutral lost
$(CH_3)_2CDCH_2CH_3^{+\cdot}$ (73)	57	81	CH_4
	56	2	CH_3D
	43	14	C_2H_6
	42	3	C_2H_5D
$(CD_3)_2CHCH_2CH_3^{+\cdot}$ (78)	62	12.5	CH_4
	61	2	CH_3D
	60	0	CH_2D_2
	59	48	CHD_3
	58	2	CD_4
	48	0	C_2H_6
	47	31	C_2H_5D
	46	0	$C_2H_4D_2$
	45	3	$C_2H_3D_3$
	44	1.5	$C_2H_2D_4$
$(CD_3)_2CDCH_2CH_3^{+\cdot}$ (79)	63	8	CH_4
	62	5	CH_3D
	61	1.5	CH_2D_2 ($\dot{C}D_3$?)
	60	48	CHD_3
	59	2	CD_4
	48	31	C_2H_5D
	47	0	$C_2H_4D_2$
	46	0	$C_2H_3D_3$
	45	3	$C_2H_2D_4$
	44	1.5	C_2HD_5

[a] Values measured by peak height and normalized to a total metastable ion current of 100 units (*B*/*E* scans).

of the uncertainty concerning the loss of neutrals having nominal masses of 16 (CH_4 or $\dot{C}H_2D$) and 17 (CH_3D or $\dot{C}HD_2$), no detailed discussion of methyl radical and methane loss is presented.

(ii) The observation of $\dot{C}H_3$, CH_4 (or less probably $\dot{C}H_2D$), $\dot{C}D_3$ (or less probably CH_2D_2), and CHD_3 losses, but essentially no $\dot{C}HD_2$ (or CH_3D) loss, from [1,1,1-$^2H_3$]pentane is significant. The observed eliminations can all be accommodated satisfactorily in terms of mechanisms, analogous to those shown in Schemes IV and V, involving 1,2 shifts of intact methyl or ethyl groups followed by loss of a complete methyl group. However, in order to lose $\dot{C}HD_2$ or CH_3D, the original CD_3 group must be broken up at some stage. Most probably, the minor elimination of a neutral of mass 17 arises by CH_3D loss from an isomerized structure such as $CH_3CH_2CH(CH_3)CD_3^{+\cdot}$.

Scheme V

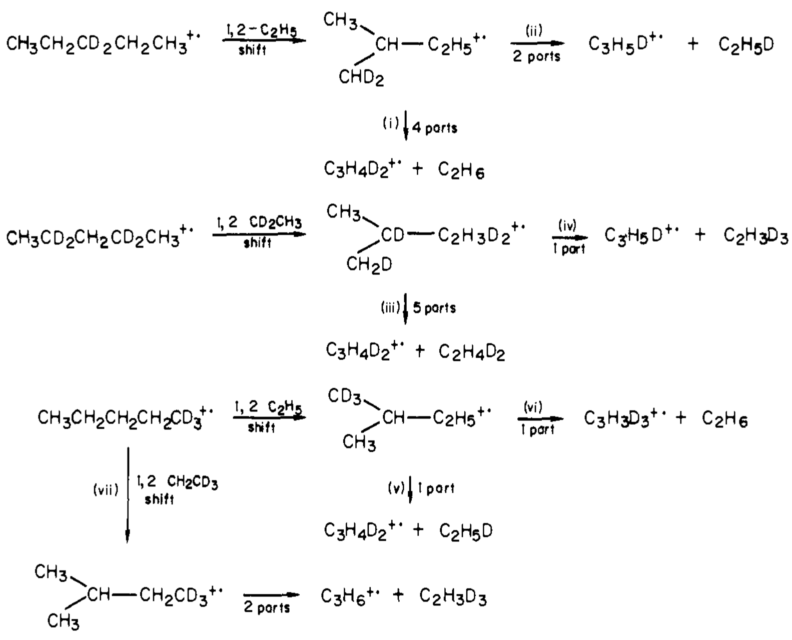


(iii) A more detailed analysis is possible for ethane loss from ionized *n*-pentane, because ethyl radical elimination is not an important side reaction. The mechanism shown in Scheme VI goes some way in explaining the labeling results. A 1,2-ethyl shift occurs (via a nonconcerted mechanism; see previous schemes for details) and the migrating ethyl group is lost, together with a hydrogen atom from either of the methyl groups in the isomerized ion. On this basis, the relative abundances of labeled ethanes, lost from a given labeled parent ion, can be calculated. In these calculations, it is assumed that in the loss of ethanes the selection of H vs. D from a methyl group does not involve an isotope effect. For $CH_3CH_2CD_2CH_2CH_3^{+\cdot}$, the calculated ratios (reaction i in competition with reaction ii, Scheme VI) are C_2H_6 67, C_2H_5D 33, $C_2H_4D_2$ 0; the observed ratios are 65:33:2.

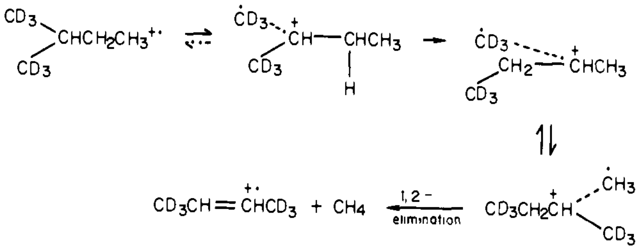
For $CH_3CD_2CH_2CD_2CH_3^{+\cdot}$, the expected ratios (reaction iii in competition with reaction iv, Scheme VI) are C_2H_6 0; C_2H_5D 0, $C_2H_4D_2$ 83, $C_2H_3D_3$ 17, $C_2H_2D_4$ 0; the observed ratios are 0:1:86:13:0. The calculated values for $CH_3CH_2CH_2CH_2CD_3^{+\cdot}$ (reactions v, vi, and vii in competition) are C_2H_6 25, C_2H_5D 25, $C_2H_4D_2$ 0, $C_2H_3D_3$ 50; the experimental data are 35:21:1:43. The labeling results agree well with those expected on the basis of the model. The reasonable agreement between the experimental and calculated data supports the assumption of a zero or small isotope effect in the loss of ethanes. The absence of a significant isotope effect is in accord with the model, since the rate-determining step precedes H or D abstraction from a methyl group. Thus, competition between H and D abstraction should occur in the presence of excess energy and greatly diminish, or remove, the potential primary detuterium isotope effect.

It is not necessary to consider further isomerization of these *i*-$C_5H_{12}^{+\cdot}$ ions (Scheme VI) to *neo*-$C_5H_{12}^{+\cdot}$ structures. This isomerization would require an activation energy to generate the complex $(CH_3)_2CHCH_2^{+}\cdots\dot{C}H_3$ which could, if attained, rearrange to $(CH_3)_4C^{+\cdot}$ via a 1,2-hydride shift. The sum $\Delta H_f[(CH_3)_2CH^+] + \Delta H_f[\dot{C}_2H_5]$ is 217 kcal mol^{-1}, which is much less than $\Delta H_f[(CH_3)_2CHCH_2^+] + \Delta H_f[\dot{C}H_3]$ (232 kcal mol^{-1}) although the energy differences of the two complexes associated with these ΔH_f values may be appreciably smaller. Nevertheless, we conclude that in metastable dissociations of directly generated $(CH_3)_2CHCH_2CH_3^{+\cdot}$, or in metastable dissociations of this ion

Scheme VI

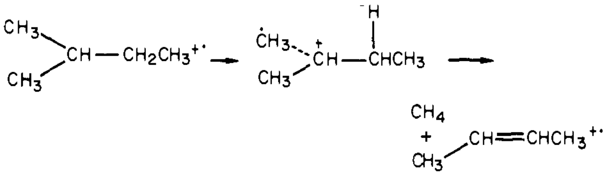


Scheme VII



generated with excess energy from ionized *n*-pentane, isomerization to *neo*-$C_5H_{12}^{+\cdot}$ should complete poorly, if at all, with dissociation of $(CH_3)_2CHCH_2CH_3^{+\cdot}$.

(b) ^2H-Labeled Isopentanes (Table III). Methane loss from ionized isopentane can be formulated as arising mainly via a 1,2-elimination (eq 2). In order to accommodate the preference for CHD_3 loss, rather than CD_4 elimination, from $(CD_3)_2CHCH_2CH_3^{+\cdot}$ and $(CD_3)CDCH_2CH_3^{+\cdot}$, it is necessary to postulate preferential transfer of a hydrogen atom from the methylene group, instead of deuterium atom transfer from the CD_3 group. This preference could arise from a deuterium isotope effect, or from the fact that a more stable $C_4H_8^{+\cdot}$ ion (ionized but-2-ene) is formed when hydrogen transfer occurs from the methylene group.

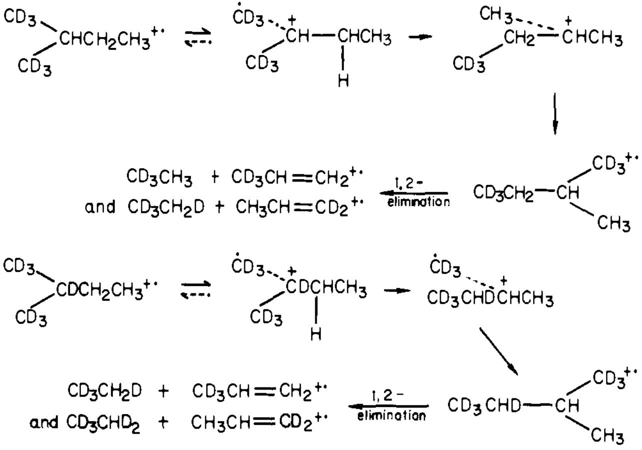


(2)

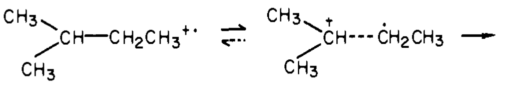
In addition to the simple 1,2-elimination discussed above, there must be at least one other mechanism whereby methane can be eliminated. This conclusion stems from the observation of a minor amount of CH_3D and CH_4 loss from $(CD_3)_2CHCH_2CH_3^{+\cdot}$ and $(CD_3)_2CDCH_2CH_3^{+\cdot}$. We propose that a 1,2-methyl shift occurs to give another isomeric isopentane radical cation (Scheme VII). As expected, the hydrogen atoms in the methylene group are preferentially involved in the eventual methane elimination.

A mechanism analogous to Scheme VII explains the increased proportion of CH_3D loss, relative to CH_4 elimination, observed for $(CD_3)_2CDCH_2CH_3^{+\cdot}$ compared to $(CD_3)_2CHCH_2CH_3^{+\cdot}$. In Scheme VII, the extra deuterium atom becomes part of the methylene group when the 1,2-CD_3 shift takes place; therefore, there is an increased probability of losing CH_3D.

Scheme VIII

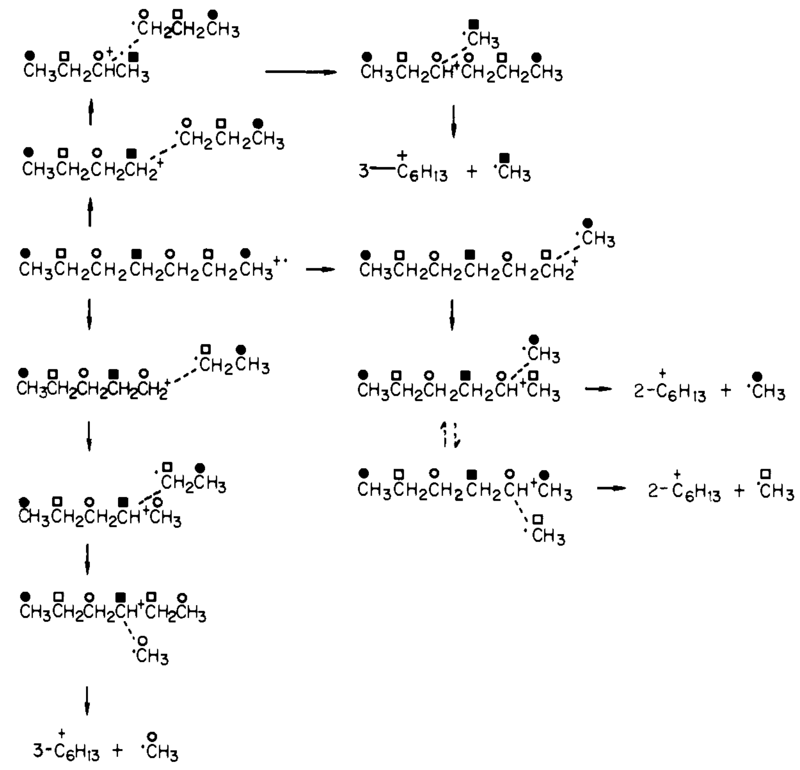


Ethane loss also occurs from ionized isopentane and may be interpreted in terms of a 1,2-elimination (eq 3). The major portion of the ethane loss can be understood in this way; thus $(CH_3)_2CDCH_2CH_3^{+\cdot}$ loses mainly C_2H_6, whereas $(CD_3)_2CHCH_2CH_3^{+\cdot}$ and $(CD_3)_2CDCH_2CH_3^{+\cdot}$ eliminate predominantly C_2H_5D. Indeed, the identical behavior of the last two ions, when undergoing ethane loss, is good evidence in favor of eq 3; the methine hydrogen atom is evidently not involved at all. However, there is clearly another (minor)) mechanism whereby ethane is lost from ionized isopentane. This is evident from the minor losses of $C_2H_3D_3$ and $C_2H_2D_4$ from $(CD_3)_2CHCH_2CH_3^{+\cdot}$ and the analogous elimination of small amounts of $C_2H_2D_4$ and C_2HD_5 from $(CD_3)_2CDCHCH_2CH_3^{+\cdot}$ (Table III). These processes can be ascribed to the occurrence of a 1,2-CD_3 shift in a minor fraction of the ions decomposing via ethane loss (Scheme VIII). After the isomerization has taken place, a CD_3CH_2- group is present in the rearranged isopentane radical cation; a 1,2-elimination (presumably nonconcerted; see eq 3) can then lead to loss of CD_3CH_3 or CD_3CH_2D from $CD_3CH_2CH(CD_3)CH_3^{+\cdot}$. On the assumption that an isotope effect of roughly 2 favors H, rather than D, transfer in the final step, the data of Table III can



(3)

Scheme IX



be explained. For example, the nonoccurrence of $C_2H_4D_2$ loss from $(CD_3)_2CHCH_2CH_3^{+\cdot}$ and the nonoccurrence of both $C_2H_4D_2$ and $C_2H_3D_3$ elimination from $(CD_3)_2CDCH_2CH_3^{+\cdot}$ are easily accommodated as shown in Scheme VIII. In addition, the minor loss of CH_3CH_2D from $(CD_3)_2CDCH_2CH_3^{+\cdot}$ can also be rationalized. This process cannot arise by loss of the initial CH_2CH_3 group because the data for $(CD_3)_2CHCH_2CH_3^{+\cdot}$ and $(CD_3)_2CDCH_2CH_3^{+\cdot}$ reveal that the methine hydrogen (or deuterium) atom does not participate in the direct loss of ethane. However, the occurrence of a 1,2-CH_3 shift in $(CH_3)_2CDCH_2CH_3^{+\cdot}$ can produce $CH_3CHDCH(CH_3)_2^{+\cdot}$ (by a parallel mechanism to that depicted in Scheme VIII); a 1,2-elimination then leads to CH_3CH_2D loss. Thus, all the data for ethane loss from ionized isopentane can be accommodated by eq 3 and Scheme VIII; most ions decompose directly, but some 15% undergo an irreversible 1,2-methyl shift prior to dissociation.

In order to test the analysis for ionized isopentane, $(CH_3)_2CHCH_2CD_3$ was synthesized subsequent to the formulation of the model. According to the model, $(CH_3)_2CHCH_2CD_3^{+\cdot}$ ought to eliminate mainly CH_4, together with a minor amount of CHD_3, and CH_3CD_3, together with a small amount of CH_3CH_3; this is observed to be the case. The methane lost is almost exclusively CH_4, with only a very minor (ca. 3%) contribution from CHD_3 elimination. The nonoccurrence of CH_3D loss is strong evidence against a significant 1,3-elimination of methane from ionized isopentane. Ethane loss from $(CH_3)_2CHCH_2CD_3^{+\cdot}$ comprises mainly CH_3CD_3 elimination, as expected from eq 3, though a small amount of CH_3CH_3 loss (ca. 15%) also occurs. These observations are in satisfactory agreement with those predicted by the model.

Ionized *n*-Heptane

It is instructive to extend the analysis of $C_4H_{10}^{+\cdot}$ and $C_5H_{12}^{+\cdot}$ to $C_7H_{16}^{+\cdot}$. Ionized *n*-heptane has been the subject of exhaustive investigation using several methods, including ^{13}C-labeling.[14] Scheme IX shows the possible isomerizations involving a 1,2-methyl, 1,2-ethyl, or 1,2-propyl shift. The cases of ethyl and propyl migrations are unambiguous: the 3- and 4-carbon atoms become methyl groups which can be lost to give a secondary hexyl cation. For the 1,2-methyl shift, preferential elimination of the migrating methyl group could occur, thus accounting for loss of the 1-carbon atom. However, in order to lose the 2-carbon atom, the 1,2-methyl shift must occur completely, followed by stretching and breaking of the bond between the original 2- and 3-carbon atoms. Such a process might well be unfavorable (as is observed for *n*-butane radical cations; see Scheme III and related discussion); consequently, elimination of the 2-carbon atom is less facile than loss of any of the other carbon atoms. Therefore, the observed ratios (26:3:18:6 at 70 eV and 30:0:18:17 at 11.5 eV) for loss of the 1, 2, 3, and 4-carbon atoms, in the methyl radical elimination, can be rationalized. Moreover, the observation[14] that $CH_3CH_2CD_2CH_2CD_2CH_2CH_3^{+\cdot}$ eliminates $\dot{C}H_3$, $\dot{C}H_2D$, and $\dot{C}HD_2$ can also be understood in terms of Scheme IX; the minor loss (7% at 70 eV) of $\dot{C}D_3$ is less easily interpreted, but this process cannot compete effectively at energies nearer threshold (0% at 11.5 eV).[14]

Similar behavior is found for other linear ionized alkanes, such as n-$C_6H_{14}^{+\cdot}$ and n-$C_9H_{20}^{+\cdot}$, where a discrimination is observed against elimination of the 2-carbon atom in $\dot{C}H_3$ loss.[14,24] This can be understood in terms of decomposition mechanisms analogous to those depicted for n-$C_7H_{16}^{+\cdot}$ in Scheme IX.

Conclusions

The unimolecular reactions of isolated $C_nH_{2n+2}^{+\cdot}$ species can be explained, in some detail, in terms of species involving a radical bound to an incipient carbonium ion. Rearrangement of the incipient carbonium ion can often precede or accompany decomposition, especially in the case of ionized *n*-alkanes. When the ionized alkane is of sufficient size, various alkyl shifts become possible; in such circumstances, extremely complex behavior frequently results. This phenomenon presumably reflects the fact that no functional groups are present in the radical cation and there is no bond that is particularly weakened by the ionization process. Consequently all the carbon–carbon bonds are significantly reduced in strength and various alkyl shifts occur, especially for ionized *n*-alkanes. For branched isomers, there is some preference for stretching the bond(s) which give rise to an incipient secondary cation, but this factor appears not to be overriding in all circumstances. The situation is often further complicated by the occurrence of deuterium isotope effects.

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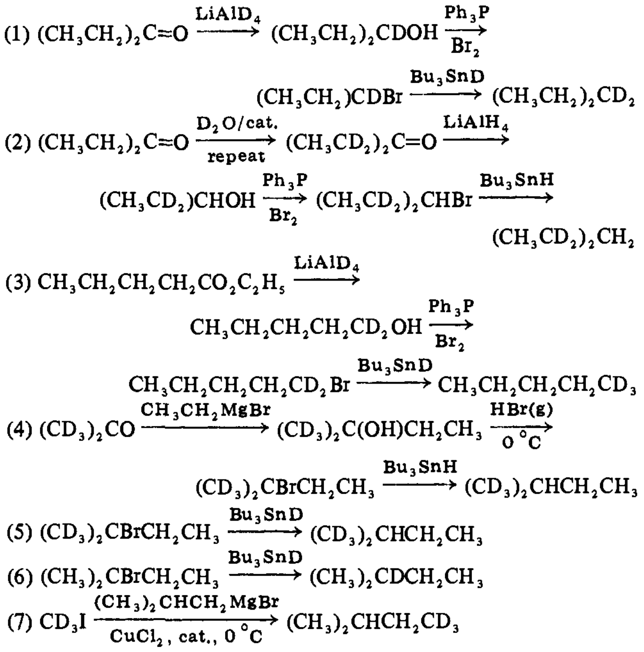
(24) A. Lavanchy, R. Houriet, and T. Gaumann, *Org. Mass Spectrom.*, **14**, 79 (1979).

Scheme X



$$(1)\ (CH_3CH_2)_2C{=}O \xrightarrow{LiAlD_4} (CH_3CH_2)_2CDOH \xrightarrow[Br_2]{Ph_3P} (CH_3CH_2)CDBr \xrightarrow{Bu_3SnD} (CH_3CH_2)_2CD_2$$

$$(2)\ (CH_3CH_2)_2C{=}O \xrightarrow[repeat]{D_2O/cat.} (CH_3CD_2)_2C{=}O \xrightarrow{LiAlH_4} (CH_3CD_2)CHOH \xrightarrow[Br_2]{Ph_3P} (CH_3CD_2)_2CHBr \xrightarrow{Bu_3SnH} (CH_3CD_2)_2CH_2$$

$$(3)\ CH_3CH_2CH_2CH_2CO_2C_2H_5 \xrightarrow{LiAlD_4} CH_3CH_2CH_2CH_2CD_2OH \xrightarrow[Br_2]{Ph_3P} CH_3CH_2CH_2CH_2CD_2Br \xrightarrow{Bu_3SnD} CH_3CH_2CH_2CH_2CD_3$$

$$(4)\ (CD_3)_2CO \xrightarrow{CH_3CH_2MgBr} (CD_3)_2C(OH)CH_2CH_3 \xrightarrow[0\ ^{\circ}C]{HBr(g)} (CD_3)_2CBrCH_2CH_3 \xrightarrow{Bu_3SnH} (CD_3)_2CHCH_2CH_3$$

$$(5)\ (CD_3)_2CBrCH_2CH_3 \xrightarrow{Bu_3SnD} (CD_3)_2CHCH_2CH_3$$

$$(6)\ (CH_3)_2CBrCH_2CH_3 \xrightarrow{Bu_3SnD} (CH_3)_2CDCH_2CH_3$$

$$(7)\ CD_3I \xrightarrow[CuCl_2,\ cat.,\ 0\ ^{\circ}C]{(CH_3)_2CHCH_2MgBr} (CH_3)_2CHCH_2CD_3$$

Experimental Section

The mass spectra were determined using a Kratos-AEI MS 50 double-focusing mass spectrometer operating at a source pressure of ca. 10^{-7} Torr. Ionization was effected by electron impact using an electron beam having a nominal energy of 70 eV. All daughter ions arising from decomposition of a given parent ion were recorded by scanning the magnetic and electric field simultaneously, such that their ratio remained constant.[25]

All unlabeled compounds were available commercially and were used without further purification. Labeled compounds were synthesized by the routes shown in Scheme X. These routes are exemplified by the following procedures.

Step 1. [3,3-$^{2}H_{2}$]Pentane. Pentan-3-one (4.3 g) was added to a stirred suspension of 0.5 g of $LiAlD_4$ in 10 mL of dry diethyl ether; the mixture was stirred for 1 h, 10 mL of H_2O was added, and the ether layer was separated and fractioned to give 2.7 g (63%) of [3-$^{2}H_{1}$]pentan-3-ol (bp 108–116 °C). The resultant alcohol was dissolved in 20 mL of dry dimethylformamide containing 8.5 g of triphenylphosphine and titrated with bromine until a yellow-red color persisted. Steam distillation and drying afforded 2.9 g (64%) of 3-bromo[3-$^{2}H_{1}$]pentane; 1.8 g of bromide was taken and added immediately to 3.5 g of neat tributyltin deuteride (Bu_3SnD); [3,3-^{2}H]pentane was distilled off, as it was formed, within a few minutes.

Step 4. [2-*methyl*-$^{2}H_{3}$-1,1,1-$^{2}H_{3}$]Butane [$(CD_3)_2CHCH_2CH_3$]. A solution of ethylmagnesium bromide was prepared from 1.0 g of Mg and 4.4 g of CH_3CH_2Br in 25 mL of dry ether; to this solution was added 2.5 mL of $(CD_3)_2CO$ in 5 mL of dry ether. After stirring overnight, hydrolysis was effected with 10 mL of saturated ammonium chloride solution; the ether was removed by distillation to leave [2-*methyl*-$^{2}H_{3}$-1,1,1-$^{2}H_{3}$]butan-2-ol. This alcohol was treated with gaseous HBr at 0 °C until saturated and maintained at −10 °C for 4 days. The upper layer of bromide was separated, dried (K_2CO_3), filtered, and reacted directly with Bu_3SnH (1 g of bromide with 1.8 g of Bu_3SnH) as before.

Step 7. 2-Methyl[4,4,4-$^{2}H_{3}$]butane [$(CH_3)_2CHCH_2CD_3$]. A solution of isobutylmagnesium bromide was prepared from 2.0 g of Mg and 12.5 g of $(CH_3)_2CHCH_2Br$ in 50 mL of dry tetrahydrofuran; the solution was cooled to 0 °C and 0.5 g of $CuCl_2$ was added with stirring; 10 mL of dry hexamethylphosphoramide then was added during 15 min while maintaining the temperature below 5 °C. To this stirred suspension was added 5 g of CD_3I in 10 mL of dry tetrahydrofuran, while maintaining the temperature between 0 and 5 °C. After 30 min the reaction flask was warmed to 50 °C and the volatile products were collected in a dry ice/acetone trap. Redistillation at atmospheric pressure afforded 0.9 g (35%) of 2-methyl[4,4,4-$^{2}H_{3}$]butane (bp 27–29 °C).

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[25] A. P. Bruins, K. R. Jennings, and S. Evans, *Int. J. Mass Spectrom. Ion Phys.*, **26**, 395 (1978).