accessible and of comparable stability. One important reason for the difference often observed between the reactions in the ion source and the reactions of metastable ions is that distonic ions, as stable forms or as reactions intermediates, are prominent among the long-lived, low-energy ion population.

Acknowledgment. The encouragement and support from Prof. Dr. H.-Fr. Grützmacher and the expert technical assistance from Mr. E. Gärtner are gratefully acknowledged.

Registry No. 3, 114377-13-8; **4a**, 114377-14-9; **5a**, 114377-15-0; **6a**, 114377-16-1; **7a**, 114377-17-2; **8a**, 114377-18-3; **9**, 114377-19-4; **9a**, 114377-20-7; **10**, 114377-21-8; **11**, 114377-22-9; **12**, 114377-23-0; **13**, 53925-78-3; **14**, 20694-03-5; **15**, 20694-06-8; **16**, 114377-24-1; **17**, 114377-25-2; **18**, 20694-02-4; **18b**, 70677-54-2; **19**, 70677-54-2; **19b**, 114377-27-4; **20**, 20694-07-9; **20b**, 99033-68-8; i-PrO(CH$_2$)$_2$NHCH$_3$, 114377-28-5; i-PrOCH$_2$CD$_2$NHC$_2$H$_5$, 114377-29-6; i-PrOCH$_2$CH$_2$CD$_2$NHC$_3$H$_7$, 114377-30-9; i-PrOCH$_2$CD$_2$NHC$_4$H$_9$, 114377-31-0; i-PrOCH$_2$CD$_2$NHC$_5$H$_{11}$, 114377-32-1; i-PrOCH$_2$CD$_2$NHC$_6$H$_{13}$, 114377-33-2; i-PrO(CH$_2$)NHCH(CH$_3$)$_2$, 114377-34-3; i-PrOCH$_2$CD$_2$NHCH(CH$_3$)$_2$, 114377-35-4; i-PrO(CH$_2$)$_2$NHC(CH$_3$)$_3$, 114377-36-5; i-PrO(CH$_2$)$_2$N(CH$_3$)$_2$, 71126-59-5; i-PrO(CH$_2$)$_2$N(CH$_3$)C$_5$H$_{11}$, 114377-37-6; PhCH$_2$OCH(CH$_3$)CH$_2$NH$_2$, 6449-46-3; PhCH$_2$OCH$_2$CH(CH$_3$)NH$_2$, 114377-38-7; PhCH$_2$OC(CH$_3$)$_2$CH$_2$NH$_2$, 114377-39-8; PhCH$_2$OCH$_2$C(CH$_3$)$_2$NH$_2$, 114377-40-1; CH$_3$(CH$_2$)$_4$CH(NH$_2$)CH$_2$CH$_3$, 24552-04-3; PhCH$_2$O(CH$_2$)$_3$NH$_2$, 16728-64-6; PrNH$_2$, 107-10-8; i-PrO(CH$_2$)$_3$N(CH$_3$)$_2$, 71126-66-4; PrNMe$_2$, 926-63-6; PhCH$_2$OCH$_2$CH(CH$_3$)CH$_2$NH$_2$, 114377-41-2; (CH$_3$)$_2$CHCH$_2$NH$_2$, 78-81-9.

Secondary Hydrogen Isotope Effects on Simple Cleavage Reactions in the Gas Phase: The α-Cleavage of Tertiary Amine Cation Radicals

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Abstract: Intramolecular secondary hydrogen isotope effects on the α-cleavage reaction of 14 unsymmetrically deuterium labeled tertiary amine cation radicals have been determined in order to probe the variation of the isotope effect with the distance to the rupturing carbon–carbon bond, with the structure of the radical lost, and with the internal energy of the reactant. The low-energy molecular ions exhibit normal isotope effects (i.e., predominant loss of the unlabeled alkyl radical), which are highest for β-labeled ions (1.30 per deuterium) and decrease with increasing distance between the isotopic label and the point of rupture; significant effects are observed even for deuterium substitution four bonds removed (1.04 per deuterium for ϵ-labeled ions). The isotope effects are relatively small and normal for molecular ions with high internal energy, with one exception: the secondary isotope effect on the fast (ion-source) reactions of the δ-labeled *N*-methyldipentylamine is inverse (0.98 per deuterium). The structure of the alkyl radical lost seems not to have a pronounced influence on the secondary isotope effects.

Isotope effects are often encountered in studies of the reactions of gaseous positive ions.[1,2] Structural and mechanistic information has in most instances been derived from the observation of primary hydrogen isotope effects; conclusions have, in some cases, been based on the (implicit) premise that secondary isotope effects are generally relatively small and can be neglected. This may often not be a valid assumption, given that appreciable secondary isotope effects have been reported in a number of instances.[1,3–15] In particular, relatively large intramolecular secondary isotope effects have been described for loss of methyl radicals from the molecular ions of alkylbenzenes,[5,15] for elimination of methane from the propane and 2-methylpropane cation radicals,[13] and for elimination of methane from *tert*-butoxide ions in the gas phase.[14]

Isotope labeling influences the rates of the reactions of cation radicals, in many cases through a combination of primary and secondary isotope effects. Mechanistic conclusions often depend on the ability to distinguish between the relative contributions from primary and secondary effects, but a quantitative distinction can be difficult; even qualitative estimates can be difficult to make, in the absence of systematic experimental studies of secondary hydrogen isotope effects. We have therefore investigated the influence of deuterium substitution on simple cleavage reactions of cation radicals, to determine the variation of secondary hydrogen isotope effects with the distance to the bond cleavage, with the structure of the alkyl radical lost, and with the internal energy

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0002-7863/88/1510-3869$01.50/0

Table I. Intramolecular Secondary Hydrogen Isotope Effects on the α-Cleavage of Unsymmetrically Deuterium Labeled *N*-Methyldipentylamine Cation Radicals

	compound	label position	isotope effects[a] 70 eV	15 eV	10 eV	CID (20%)[b]	CID (50%)[b]	1st FFR	2nd FFR[c]
1	$C_5H_{11}N(CH_3)CD_2CH_2CH_2CH_2CD_3$	α	1.01_4	1.02_6	1.04_4			1.07_4	1.08
2	$C_5H_{11}N(CH_3)CH_2CD_2CH_2CH_2CH_3$	β	1.03_4	1.05_1[d]	1.15_7	1.07_1	1.09_2	1.19_2	1.30
3	$C_5H_{11}N(CH_3)CH_2CH_2CD_2CH_2CH_3$	γ	1.03_1	1.02_6	1.03_0		1.06_0	1.08_9	1.09_9
4	$C_5H_{11}N(CH_3)CH_2CH_2CH_2CD_2CH_3$	δ	0.98_6	0.98_4	0.97_9	1.01_7	1.01_9	1.03_1	1.03_7
5	$C_5H_{11}N(CH_3)CH_2CH_2CH_2CH_2CD_3$	ϵ	1.00_3	1.00_4	1.00_6			1.03_7	1.03_6

[a] Isotope effects per deuterium (cf. ref 28). [b] Attenuation of the main beam intensity to 50 and 20% of the initial value. [c] Measured on the unusually large mass spectrometer (see Experimental Section); experimental abundance ratios: 1.29_5 (**1**), 1.71_6 (**2**), 1.21_9 (**3**), 1.08_6 (**4**), 1.12_2 (**5**). [d] The values for electron energies between 15 and 10 eV are the following: 1.06_1 (14 eV), 1.08_6 (13 eV), 1.11_2 (12 eV), and 1.15_2 (11 eV).

of the reacting ions. A preliminary account of part of this work has appeared.[12]

A direct measure of intramolecular secondary hydrogen isotope effects on simple cleavage reactions can be obtained from the relative ion yield for loss of identical (apart from deuterium labeling) radicals from symmetrical substrates. The α-cleavage of tertiary aliphatic amine cation radicals was chosen as a prototype simple cleavage. This reaction proceeds in high ion yield in the mass spectrometer ion source as well as in the field-free regions, almost without competing reactions. It is known that the loss of radicals from molecular ions is in some cases preceded by hydrogen migration or by skeletal rearrangement,[16] and low energy primary and secondary amine cation radicals are known to exchange hydrogen atoms between the amino group and remote methylene groups in the alkyl chains prior to fragmentation.[17-20] However, the available evidence indicates that the α-cleavage of tertiary aliphatic amines is a straightforward simple cleavage reaction even at long ion lifetimes.[17,21] In particular, the MIKE spectra of the 14 deuterium labeled tertiary amines examined here show no evidence at all for intramolecular hydrogen atom abstraction or exchange in the molecular ions.

Experimental Section

The relative ion yield for the competing α-cleavage reactions in the ion source and in the first field free region (1st FFR) was determined with a VG 70-70F mass spectrometer. The accelerating voltage was 8 kV and the ionizing electron energy approximately 10, 15, or 70 eV. The abundance ratios were obtained as averages of 10 to 20 measurements, and the ion source measurements were corrected for incomplete labeling determined from low energy mass spectra. The results for the reactions in the 1st FFR, including the results for collision-induced reactions (collision gas He), were acquired by B/E scans after ionization with 70-eV electrons. The relative ion yield of the ions formed by α-cleavage in the second field free region (2nd FFR) was measured with an unusually large double focusing mass spectrometer of reverse geometry in which the distance between the analyzers is 2.7 m.[22,23] The electron energy was 70 eV and the accelerating voltage 8 kV. The measurements were performed with a wide β-slit setting and the relative ion yield was obtained from the ratio of the peak heights. Measurement of relative peak areas in spectra recorded with a narrow β-slit gave identical results within experimental error. The ratios measured for reactions in the 2nd FFR have been corrected for difference in the fractional transmittance for product ions of different masses.[23] The experiments were performed on several occasions with up to 30-month intervals and identical results were obtained.

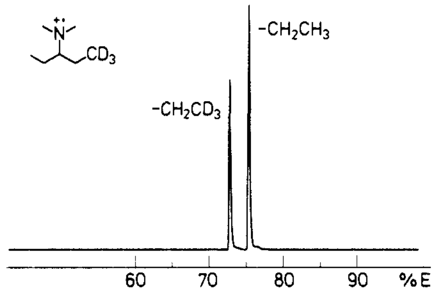


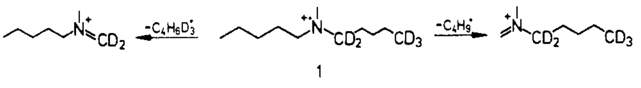
Figure 1. MIKE spectrum of compound **13**.

Table II. Intramolecular Secondary Hydrogen Isotope Effects on the α-Cleavage of Unsymmetrically Deuterium Labeled Amine and Hydrazine Cation Radicals

	compound	label position	isotope effects, 2nd FFR[a]
6	$C_4H_9N(CH_2CH_3)CD_2CD_3$	α	1.09_3
7	$C_4H_9N(CH_2CH_3)CH_2CHD_2$	β	1.31_8
8	$C_4H_9N(CH_2CH_3)CH_2CD_3$	β	1.30_5
9	$(CH_3)_2CHCH_2CH_2N(CH_3)CH_2CD_2CH(CH_3)_2$	β	1.29_2
10	$(CH_3)_2CHCH_2CH_2N(CH_3)CH_2CH_2CD(CH_3)_2$	γ	1.10_6
15	$CH_3CH_2(CD_3CH_2)CH\text{-}NH\text{-}N(CH_3)_2$	γ	1.04
16	$CH_3CH_2CH_2(CH_3CD_2CH_2)CH\text{-}NH\text{-}N(CH_3)_2$	γ	1.05

[a] See Table I, footnotes *a* and *c*.

Scheme I



The results have not been corrected for possible mass-dependent discrimination by the electron multiplier, which was operated with a post-acceleration of approximately 2 kV. Multiplier-induced errors arise from the difference in kinetic energy of the impacting ions. On the basis of the figure published by laLau[24] the discrimination is estimated to be less than 1% for the isotope effects on reactions in the 2nd FFR.[25]

Synthesis. The labeled *N*-methyldialkylamines were prepared by reaction between a suitably labeled Grignard reagent and *N*-methoxy-*N*-methylalkylamines,[26] or by reduction of the appropriate tertiary amide

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(21) Rearrangement of amine cation radicals by intramolecular hydrogen atom abstraction leads to distonic ions. The distonic isomers of primary amine cation radicals are more stable than their conventional isomers, whereas tertiary amine cation radicals are more stable than their distonic counterparts (see: Yates, B. F.; Bouma, W. J.; Radom, L. *Tetrahedron* **1986**, *42*, 6225–6234; Yates, B. F.; Radom, L.; *J. Am. Chem. Soc.* **1987**, *109*, 2910–2915; and ref 17c).

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(25) As an example, multiplier discriminiation may cause the measured *m/z* 116:114 abundance ratio for compounds **2–4** to be too high by a factor of 1.016; the isotope effect per deuterium presented in the tables may in turn be too high by a factor of 1.008. Lower molecular weight parent ions may give rise to slightly larger errors.

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Table III. Intramolecular Secondary Hydrogen Isotope Effects on the α-Cleavage of Tertiary Amine Cation Radicals Unsymmetrically Labeled with Deuterium at the γ Position

		isotope effects[a]						
	compound	70 eV	15 eV	10 eV	CID (20%)[b]	CID (50%)[b]	1st FFR	2nd FFR[c]
11	$CH_3CH_2CH_2N(CH_3)CH_2CH_2CD_3$	1.00_3	1.00_0	1.00_8	1.05_3	1.06_3	1.08_7	1.10_6
12	$(CH_3)_2CHCH_2N(CH_3)CH_2CH(CD_3)_2$	1.01_4	1.03_8	1.02_9	1.04_4	1.05_2	1.09_4	1.10_7
13	$CH_3CH_2(CD_3CH_2)CHN(CH_3)_2$	1.02_9	1.02_3	1.03_0		1.08_1	1.10_3	1.13_7
14	$CH_3CH_2CH_2(CH_3CD_2CH_2)CHN(CH_3)_2$	1.01_8			1.05_2	1.06_2	1.08_0	1.08_6

[a] See Table I, footnote *a*. [b] See Table I, footnote *b*. [c] See Table I, footnote *c*.

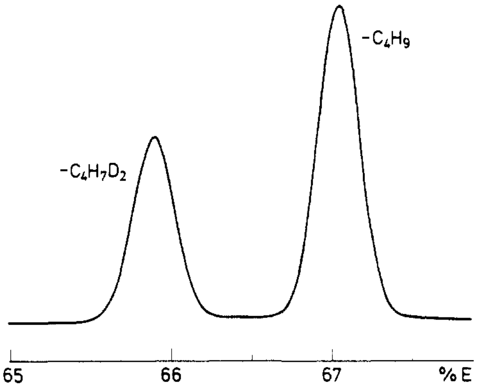


Figure 2. The α-cleavage peaks in the MIKE spectrum of compound **2**.

with $LiAlH_4$ or $LiAlD_4$. The labeled *N*,*N*-dimethylalkylamines were prepared by reductive amination of labeled ketones with $(CH_3)_2NH$ and $NaBH_3CN$.[27] The compounds were purified by distillation or preparative gas chromatography and their identity ascertained by mass spectrometry.

Results

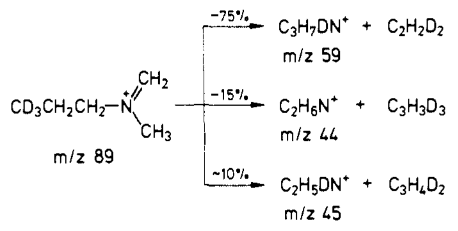
The molecular ions of the tertiary amines studied react nearly exclusively by simple α-cleavage in the ion source and in the field-free regions (see Figure 1).

The results presented in Tables I–III are derived from the corrected (see Experimental) relative ion yield for the competing α-cleavage reactions of unsymmetrically labeled tertiary amine molecular ions (Scheme I). To facilitate comparisons, the effects are given as isotope effects per deuterium, assuming a multiplicative relationship.[28] The results for **7** and **8** support the validity of this assumption.

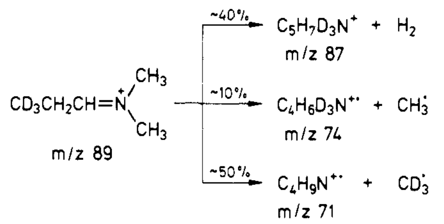
Metastable Ions. The instrumentation used in the present study for 2nd FFR measurements allows determination of relative ion yields for the competing α-cleavage reactions with considerably improved precision and accuracy compared to our measurements for metastable ions decomposing in the 2nd FFR of an MS902 mass spectrometer.[12] The agreement is nonetheless quite good, considering that the earlier results were not corrected for instrumental discrimination.

Loss of alkyl radicals from the molecular ions in the 2nd FFR gives rise to Gaussian-shaped metastable peaks (Figure 2). The translational energy released in the reactions under study is between 12 and 20 meV ($T_{0.5}$), with no difference between the energies released in the two competing α-cleavages for any of the unsymmetrically deuterium labeled precursor ions.

Scheme II



Scheme III



Loss of the unlabeled alkyl radical predominates in the μs reactions of all tertiary amine molecular ions examined. The effect of isotopic substitution decreases with increasing distance to the point of rupture, but only limited variation is encountered for a given position of the isotopic label. The isotope effect per deuterium is ca. 1.09 for α-labeled amines, ca. 1.30 for β-labeled amines, and ca. 1.10 for γ-labeled amines, regardless of the number of deuterium atoms present and regardless of the identity of the alkyl radical expelled. An exception is the isotope effect on the loss of ethyl radicals from **13**.

The α-CD_2 groups in **1** and **6** are retained in the ionic fragment in either α-cleavage reaction (see Scheme I); an additional label has been introduced to distinguish between the two C–C cleavage reactions. The results reported for **1** and **6** are corrected[28] for the effect of the additional labeling (cf. compounds **5** and **8**).

The isotope effects measured for reactions in the 1st FFR of the VG 70-70 instrument are close to those measured for reactions in the 2nd FFR of the unusually large mass spectrometer, with the exception of the results for **2**. However, the two sets of results should be compared with caution; the measurements for the 1st FFR pertain to ions decomposing an order of magnitude more rapidly,[29] and these results have not been corrected for any effects of instrumental discrimination. There should not be any reason why measurements using B/E scans would not yield reliable abundance ratios for competing reactions, given that the translational energy released is the same for the processes under study, as is the case here.

Ion-Source Reactions. The difference in relative ion yield for the competing α-cleavage reactions in the ion source increases with decreasing ionizing energy for the α- and β-labeled amine molecular ions (**1** and **2**), whereas only marginal variation is observed for the remaining compounds. The immonium ions formed by α-cleavage in the ion source of *N*-methyldialkylamines react further by alkene elimination reactions that involve hydrogen migration (Scheme II); the immonium ions formed from *N*,*N*-dimethylalkylamines react as shown in Scheme III.[30–33]

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(27) Birch, R. F.; Bernstein, M. D.; Durst, H. D. *J. Am. Chem. Soc.* **1971**, *93*, 2897–2904.

(28) The isotope effect per deuterium for dideuteriated species is obtained as the square root of the corrected relative ion yield, for trideuteriated species as the cube root of the corrected relative ion yield. The isotope effect for species labeled at more than one position is obtained by dividing the observed relative ion yield by the relative ion yield for the corresponding singly labeled species. For example, the effect of the α-deuterium atoms in the α,α,ε,ε-labeled compound, **1**, is obtained as the ratio of the corrected relative ion yields measured for **1** and **5**: the effect per α-deuterium atom is the square root of this ratio.

(29) The lifetime of a parent ion with *m*/*z* 100 is 1–2 μs for reactions in the 1st FFR of the VG 70–70 instrument and 20–40 μs for reactions in the 2nd FFR of the unusually large mass spectrometer.

(30) Djerassi, C.; Fenselau, C. *J. Am. Chem. Soc.* **1965**, *87*, 5752–5756.

(31) (a) Bowen, R. D.; Williams, D. H.; Hvistendahl, G.; Kalman, J. R. *Org. Mass Spectrom.* **1978**, *13*, 721–728. (b) Bowen, R. D.; Williams, D. H. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1064–1071. (c) Bowen, R. D. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1219–1227.

Fragmentation of the immonium ions in the ion source gives rise to abundant product ions at 70 eV, and isotope effects on these reactions, which deplete the immonium ion population, may influence the relative abundance of the immonium ions leaving the ion source. However, immonium ion fragmentation is negligible at 10 eV ionizing energy, and the results obtained from low-voltage mass spectra hence reflect almost exclusively the influence of isotopic substitution on the competing α-cleavage reactions in the ion source.

The presence of deuterium at the α-, β-, γ-, and ϵ-positions in *N*-methyldipentylamine results in preferential loss of unlabeled butyl radicals from the molecular ions. By contrast, the ion-source reactions of the δ-labeled ion, **4**, exhibit an inverse isotope effect, irrespective of ionizing energy, leading to preferential loss of $C_4H_7D_2^{\bullet}$ radicals. This result has been reproduced on four different mass spectrometers. The ion-source reactions of all γ-iabeled ions examined show a slight preference for loss of the unlabeled radical.

Collision-Induced Reactions. The isotope effects for the collision-induced reactions of the molecular ions of **2**, **3**, and **4** (formed by 70-eV ionization) are smaller than the effects measured for the reactions of metastable ions, but larger than those observed for ion-source reactions after 70-eV ionization. For **2**, the isotope effect is about the same as that observed after low-energy ionization, whereas the remaining ions examined show somewhat larger effects. In particular, the collision-induced reactions of **4** do not mimic the ion-source behavior, that is, they do not result in preferential loss of the labeled butyl radical.

Discussion

According to the RRKM theory the relative rates of two competing unimolecular reactions of an isolated species will be subject to a kinetic isotope effect when the isotopic substitution changes the number of energy states, $G^*(E - E_0)$, for one or both transition states. At low internal energies such a change will predominantly reflect that the critical energies, E_0, for the two reactions differ as the result of the effect of isotopic substitution on the zero-point energies of the transition states (eq 1).[1,34,35] Competing reactions of a symmetrical (apart from deuterium

$$\frac{k_H(E)}{k_D(E)} = \frac{G^*(E - E_{0,H})}{G^*(E - E_{0,D})} \tag{1}$$

labeling) species will hence exhibit a kinetic isotope effect if isotope-dependent modes are involved in the change in bonding when the transition states are formed; intramolecular secondary hydrogen kinetic isotope effects can, in turn, be used as a delicate probe of the detailed mechanism of simple cleavage reactions. It is worth noting that similarly detailed information cannot easily be derived from the observation of intermolecular isotope effects.[1]

Isotope effects on ion abundances will be very close to the kinetic isotope effects when a narrow interval of internal energies is sampled, as is the case for the reactions of metastable ions. Results obtained for ion-source reactions and for collision-induced reactions represent isotope effects averaged over a broad distribution of internal energies.

Intramolecular secondary isotope effects increase with decreasing internal energy of the reacting species, since the differences in zero-point energy will be relatively more important for reactions occurring near threshold. In keeping with this, the largest effects are found for the reactions of metastable ions (cf. Tables I and III). The variation in relative abundances observed when the ionizing energy is changed also reflects the energy dependence of the isotope effect.

In the collision-induced reactions, the isotope effect decreases when the main-beam intensity is reduced from 50% to 20% of the initial value, reflecting an increase in the relative abundance of ions with high internal energies. It is worth noting that the isotope effects observed in the collision experiments are uniformly higher than those observed after 70-eV ionization, indicating that the average internal energy of the amine cation radicals reacting after collisional energy transfer is less than the average energy of the ions formed by interaction with 70-eV electrons.

The observation of appreciable, normal secondary isotope effects on the α-cleavage in the 2nd FFR for all 14 labeled tertiary amines examined implies a decrease, in each case, of vibrational frequencies sensitive to isotopic substitution when the transition state is formed. It follows that a considerable number of vibrational modes is involved when the C–C bond is broken, and definitive assignment of the origin of the isotope effect is hence difficult, particularly when deuterium is introduced at positions well removed from the bond broken.[36]

Variations with Label Position. The deuterium atoms in the α- and β-positions in **1**, **2**, and **6–9** are one bond removed from the point of cleavage. The isotope effect is considerably lower when the deuterium is at the amine α-carbon (1.09 per D) than when the β-position is labeled (1.30 per D), that is, the overall change of isotope-dependent modes is less when deuterium is attached to the $N{=}CH_2$ group of the incipient ionic fragment than when the deuterium atoms are bonded to the free-radical carbon of the alkyl fragment expelled. The vibrational frequencies for C–H stretching modes for hydrogen atoms bonded to doubly bonded carbon atoms, as well as those for hydrogen atoms bonded to free-radical carbon atoms, are known to be higher than the C–H stretching frequencies for saturated methylene groups.[37,38] This would seem to imply that C–H stretching frequences in the transition state are unlikely to be lower than those in the reactant ion. The vibrational mode often assumed to be primarily responsible for secondary hydrogen isotope effects on $sp^3 \rightarrow sp^2$ transformations is the CH_2 scissoring mode that turns into the umbrella motion of the incipient $=CH_2$ and $-CH_2^{\bullet}$ groups.[14,39] The corresponding frequency is lower in the product than in the reactant ion; it seems reasonable to assume that it is already lowered in the transition state. Furthermore, the vibrational frequency associated with the umbrella motion is in all likelihood lower for $-CH_2^{\bullet}$ than for $=CH_2$; this difference might well also exert itself in the transition state, leading to a higher secondary isotope effect when deuterium is introduced at the incipient radical methylene group rather than at the immonium methylene group, in agreement with experiment.

Deuterium atoms in the γ-position, two bonds removed from the point of cleavage, give rise to normal isotope effects, considerably lower than those caused by β-deuterium atoms. The isotope effect per deuterium is virtually the same for the γ-labeled compounds examined, regardless of the extent of isotopic substitution, viz., compounds **3**, **10**, and **12**, which incorporate two, one, and six γ-deuterium atoms, respectively, all exhibit isotope effects of 1.10 per D for reactions occurring in the 2nd FFR. Similar values are found for **11** and **14**, whereas **13** shows a somewhat higher

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(32) Minor amounts of ions with *m/z* values of 59, 58, 45, and 44 are also formed from metastable $CD_3CH_2CH{=}N(CH_3)_2$ ions. The metastable $CH_3CD_2CH_2CH{=}N(CH_3)_2$ ions (*m/z* 102) fragment in the field free region mainly with formation of ions with *m/z* values of 100 (loss of H_2), 87 (loss of $CH_3^{\bullet}$), 72 (loss of $C_2H_2D_2$), 71 (loss of $C_2H_2D_3^{\bullet}$), 59 (loss of C_3H_5D), and 58 (loss of $C_3H_4D_2$). Minor amounts of ions with *m/z* values of 70, 56, 47, 46, 45, and 44 are also observed. Ingemann, S.; Hammerum, S., unpublished results (see also ref 33).

(33) (a) Bowen, R. D.; Harrison, A. G. *Org. Mass Spectrom.* **1981**, *16*, 180–182. (b) Bowen, R. D. *J. Chem. Soc., Perkin Trans. 2* **1982**, 403–408.

(34) (a) Forst, W. *Theory of Unimolecular Reactions*; Academic Press: New York, 1973. (b) Robinson, P. J.; Holbrook, C. A. *Unimolecular Reactions*; Wiley-Interscience: New York, 1972.

(35) The number of equivalent pathways (σ) is identical for the competing reactions (see ref 34).

(36) A combined FIK (Field Ionization Kinetics) and RRKM study of the secondary isotope effects for the molecular ions of the labeled *N*-methyldipentylamines is in progress: Allison, C.; Derrick, P. J.; Hammerum, S.; Ingemann, S.; Kluft, E.; Nibbering, N. M. M., to be published.

(37) Wilson, E. B.; Decius, J. C.; Cross, P. C. *Molecular Vibrations*; McGraw-Hill: New York, 1955.

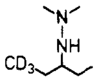
(38) (a) Pacansky, J.; Dupuis, M. *J. Am. Chem. Soc.* **1982**, *104*, 415–421. (b) Pacansky, J.; Brown, D. W.; Chang, J. S. *J. Phys. Chem.* **1981**, *85*, 2562–2567. (c) Schrader, B.; Pacansky, J.; Pfeiffer, U. *J. Phys. Chem.* **1984**, *88*, 4069–4073. (d) Chettur, G.; Suelson, A. *J. Phys. Chem.* **1987**, *91*, 3483–3488.

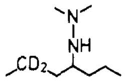
(39) (a) Streitwieser, A.; Jagow, R. H.; Fahey, R. C.; Suzuki, S. *J. Am. Chem. Soc.* **1958**, *80*, 2326–2332. (b) Halevi, E. A. *Prog. Phys. Org. Chem.* **1963**, *1*, 109–221. (c) Melander, L.; Saunders, W. H. *Reactions Rates of Isotopic Molecules*; Wiley: New York, 1980.

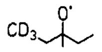
isotope effect (1.14). The vibrational frequency for the C–H stretching mode has been found to be lower for hydrogen atoms at carbon adjacent to the vacant site in alkyl radicals than for methylene groups in alkanes,[38] and this could well provide a significant contribution to the isotope effect for the γ-labeled species.

Normal isotope effects are observed for the reactions of the low-energy molecular ions of the δ- and ϵ-labeled compounds, **4** and **5**, where the hydrogen atoms are three and four bonds removed from the point of rupture: the effect is in both cases ca. 1.04 per deuterium. The available evidence does not permit us to suggest which particular isotope-dependent vibrational modes are responsible for the observed effect. The ion-source reactions of **5** exhibit a negligible isotope effect, whereas the effect observed for **4** is inverse for molecular ions of high internal energy. The slight but unmistakable preference for loss of the labeled alkyl radical shows that the number of energy states in the transition state is in this case larger for loss of the labeled radical than for loss of the unlabeled radical. The inverse isotope effect on the ion-source reactions of **4** is observed irrespective of the energy of the ionizing electrons; however, it does not show up in the collision-induced reactions, possibly reflecting that the internal energy of the molecular ions after collision is not sufficiently high.

Variation with Structure. The structure of the alkyl radical released in the α-cleavage reaction seems not to exert an appreciable influence on the secondary hydrogen isotope effect. The β-labeled species, **2** and **9**, show virtually the same isotope effect per deuterium on loss of butyl and isobutyl radicals, respectively, from the metastable molecular ions. Correspondingly, the isotope effects per deuterium for loss of ethyl, isopropyl, butyl, and isobutyl radicals from the γ-labeled compounds **11**, **12**, **3**, and **10** show very little variation. These reactions are all loss of radicals by C–C cleavage of a primary alkyl group; slightly different behavior is observed for reactions where the radical is lost from a branched carbon atom. The secondary isotope effect per deuterium on the loss of ethyl radicals from **13** is significantly higher than the isotope effect on the closely related loss of propyl radicals from **14**. We hesitate to draw firm conclusions from this result, but the loss of alkyl radicals from tertiary amines by C–C cleavage of *sec*-alkyl groups is significantly less endoergic than loss of alkyl radicals by cleavage of primary alkyl groups. The difference is estimated[40] to be ca. 35 kJ mol^{-1}; the critical energies probably vary in a similar fashion.[41] It is interesting to note that the loss of ethyl radicals in the thermal decomposition of the tertiary alkoxy radical **17** is associated with a substantially larger secondary isotope effect than is loss of isopropyl or *tert*-butyl radicals in similar thermal free-radical processes.[42]


15


16


17

Comparison with Other Systems. Eadon and Zawalski[7] have measured *inter*molecular secondary isotope effects for $I^\bullet$ loss from deuterium-labeled cyclohexyl iodides. There is no direct relationship between *inter*- and *intra*molecular isotope effects, but it is of interest that these authors also observed inverse isotope effects on the ion-source reactions of ions with remote deuterium atoms.

The similarity between the isotope effects observed for the α-cleavage of tertiary amines with the same number of bonds between the isotopic label and the point of rupture does not extend to other systems. The isotope effect on loss of alkyl radicals with deuterium at the α-carbon atom from the metastable tertiary aliphatic amines examined in the present study is higher than the secondary isotope effects reported[5,15] for methyl loss from metastable molecular ions of *tert*-butylbenzene (1.22), *tert*-butylpyridine (1.26), and isopropylbenzene (1.16). Correspondingly, γ-labeled hydrazines such as **15** and **16** (Table II) show considerably lower isotope effects than do γ-labeled amines—the isotope effects measured for reactions in the 2nd FFR for **15** and **16** are 1.04 and 1.05 per deuterium, respectively.

These differences are believed to originate to a large extent in the differences in critical energies for C–C cleavage. Higher critical energies will result in lower kinetic isotope effects, since the excess energy required for cleavage to occur at the necessary rate (ca. 10^5 s^{-1}) will increase with increasing critical energy, which in turn will diminish the difference between the number of energy states available for the two competing reactions caused by the zero-point energy difference. Isotope effects may be subject to a kinetic shift.[43]

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(40) Average value based on calculations for a number of model systems. Data for neutral species taken from the following: Pedley, J. B.; Rylance, J. *Sussex-N.P.L. Computer Analyzed Thermochemical Data: Organic and Organometallic Compounds*; Sussex University: Brighton, 1977. Schultz, J. C.; Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 3917–3927. Heats of formation for ionic species based on data from the following: Levin, R. D.; Lias, S. G. *Ionization Potential and Appearance Potential Measurements*, 1971–1981. NSRDS-NBS71, U.S. Government Printing Office; Washington. 1982. Lossing, F. P.; Lam, Y.; Maccoll, A. *Can. J. Chem.* **1981**, *59*, 2228–2231.

(41) The α-cleavage of amine cation radicals may have significant reverse critical energies, see: Hammerum, S.; Derrick, P. J. *J. Chem. Soc., Chem. Commun.* **1985**, 996–997.

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