The Dichotomy of Methyl Loss from 2-Methylalkane Molecular Ions

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The kinetic energy release for methyl loss from the molecular ion of 2-methylpentane *increases c.* twofold over the time-range 1–15 μ s. This results from a mixture of secondary and tertiary pentyl cations. The appearance energy showed that at threshold (and long times) only tertiary ions are formed. The molecular ion of 2-methylhexane produces tertiary hexyl ions by loss of methyl at threshold, but in the μ s time-frame only secondary hexyl ions appear to be formed, because the kinetic energy release is small and independent of the observation time.

INTRODUCTION

Simple carbon-carbon bond fission reactions of small alkane molecular ions generally proceed at or close to the calculated thermochemical threshold for the products formed. Thus, the molecular ions of normal alkanes (C_4-C_8) and of 2-methylpropane and 2methylbutane lose methyl to produce secondary alkyl cations with only small excess energies, ranging from 4 to 12 kJ mol^{-1} .^{1,2} However, the higher homolog, 2methylpentane, behaves differently; the threshold for the $[C_5H_{11}]^+$ ion formation is 715 kJ mol⁻¹; measured with energy-selected electrons,³ the appearance energy for $[C_5H_{11}]^+$ was 10.70 ± 0.05 eV; photoionization at 300 K yielded a value of 10.74 eV.⁴ These can only correspond to the formation of tertiary pentyl cations with 42 kJ mol⁻¹ of excess energy, because the heats of formation of the secondary and tertiary pentyl cations are known to be 748 and 673 kJ mol⁻¹, respectively.⁵ In the present paper we describe the metastable peak shapes for these fragmentations and their change with observation time.

RESULTS AND DISCUSSION

2-Methylpentane

The metastable peak shapes associated with reactions proceeding at or close to their calculated thermochemical threshold are usually of Gaussian type;⁶ for alkanes and cycloalkenes the kinetic energy releases measured at half peak height ($T_{0.5}$) are typically between 10 and 20 meV.^{1,2,7} The metastable peak shapes for [2-methylpentane]^{+.} fragmentations have been

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Table 1. Relative peak areas and kinetic energy releases $(T_{0.5}, meV)$ for reactions of 2-methylpentane									
	MS	902S	ZAB	-2F ^b					
Fragment lost	Area	T _{0.5} °	Area	Т _{0.5} с					
CH3	5	17.4	2.5	29					
CH₄	10	28.8	3.5	30					
C ₂ H ₅	57	20.2	65	22					
C_2H_6	28	18.6	29	20.5					
^a Kratos AEI first field fre ditions see I ^b VG ZAB-2 analysed io	MS 9 e regio Ref. 2. F ma: n kine	02S ma on; for e ss spec tic ener	ss specti xperimer trometer gy (MIKI	rometer, ntal con- , mass- E) spec-					

measured at short time (mean ion lifetime $\approx 1 \ \mu$ s) and at long observation time (mean ion lifetime $\approx 15 \ \mu$ s)⁸; see Table 1 for experimental conditions.

trum; for experimental conditions see Ref.

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° ±3% STD.

The metastable peak shapes for loss of methyl measured at both short and long observation time are of similar complex-Gaussian shape,⁶ with steep sides and a rounded top (n > 2.2 at all heights;⁶ the calculated n(T) curve¹⁰ further substantiates the complexity of the shape). The $T_{0.5}$ value measured is about twice as large at the long observation time than at short time. This is unusual, because the tendency is generally that a marked diminution of $T_{0.5}$ is observed for ions decomposing at longer times cf. Ref. 6. The metastable peaks for the other reactions of 2-methylpentane, loss of CH₄, C₂H₅ and C₂H₆, do not differ significantly between short and long time neither with regard to shape or kinetic energy release (the $T_{0.5}$ values differ by less than 3%).

These results show that the metastable peak associated with the methyl loss consists of a narrow and a broad component. The relative proportions depend on the molecular ion lifetime in such a way that the formation of *sec*-pentyl cations corresponds with the

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Scheme 1

narrow component and the broad component corresponds to the formation of the more stable *tert*-pentyl cation. That formation of *tert*-pentyl cations should be favoured at long times is compatible with a more complex route for attaining the dissociating step and hence a slow rising $k(E) \vee E$ curve for $[tert-pentyl]^+$ formation, while the formation of *sec*-pentyl cations is favoured at short times, compatible with their straightforward formation by a simple C—C bond fission and a relatively steep $k(E) \vee E$ curve.

The dichotomy of methyl loss from the 2methylpentane molecular ion may be visualized as shown in Scheme 1. Fission of the C(1)-C(2) bond produces the sec-pentyl cation (cf. Ref. 11). The formation of the tert-pentyl cation may be produced via an intermediately formed 2,2-dimethylbutane-like ion, which then loses methyl. This could proceed by rearrangement of the (C(4)+C(5)) fragment from C(3) to C(2) (a 1,2-ethyl shift) concomitant with a 1,2-H shift from C(2) to C(3) either in a stepwise or concerted manner; alternatively the first step could be seen as involving a complex between the sec-pentyl cation and a methyl radical¹² followed by isomerization of $[sec-pentyl]^+$ to the more stable $[tert-pentyl]^+$ (it is known that [sec-butyl]⁺ can isomerize to the more stable [tert-butyl]⁺ at long times¹³), recombination of [tert-pentyl]⁺ with methyl then forms the quaternary molecular ion. For the purpose of comparison the molecular ion of 2,2-dimethylbutane itself shows weak metastable losses of methyl, ethylene, ethyl, propyl (ZAB-2F ethane and mass spectrometer).

An alternative route to $[tert-pentyl]^+$ formation via an intermediate 2,3-dimethylbutane-like molecular ion, which could be formed by a 1,2-methyl shift from C(4) to C(3) or a 1,2-sec-propyl shift from C(3) to C(4) can be ruled out, because 2-methylpentane-5,5,5- d_3 does not lose CD₃ at long times (ZAB-2F) nor at very short (sub μ s) times (ion source).

Observations obtained for a number of deuteriated 2-methylpentanes (Table 2) support rearrangement to a 2,2-dimethylbutane-like molecular ion before loss of methyl. The molecular ion of 2-methylpentane-4,4- d_2 loses some CH₃D; this points to formation of a 2.2dimethylbutane-3,3- d_2 -like ion prior to elimination of methane. Elimination of C_2H_5D from the molecular ion of 2-methylpentane-1, $1, 1-d_3$ is similarly consistent with an intermediate 2,2-dimethylbutane-1,1,1- d_3 molecular ion. One alternative route would be that elimination of C_2H_5D occurs from a 3-(trideuteriomethyl)pentane ion formed by a 1,2-methyl shift from C(2) to C(3);^{2,14} however, the corresponding molecular ion loses C₂H₆ exclusively.

Methyl loss shows a secondary α -hydrogen isotope effect, which increases at longer times (see Table 2); the isotope effect is compatible with rate-determining fission of the C(1)—C(2) bond. The apparent isotope effect is 1.7 per D ($\sqrt[3]{5}$) at short times and nearly 2.0 per D ($\sqrt[3]{8}$) at the long observation time; this would be close to 1.6 per D ($\sqrt[3]{4}$), however, if the loss was preceded by complete rearrangement to a 2,2dimethylbutane-like ion. This is supported by measurements of the kinetic energy releases; the difference in $T_{0.5}$ values of CH₃[•] and CD₃[•] loss is larger than 30% at short time relative to less than 10% at long observation time, which is compatible with a rate of rearrangement in the same order as the time window of the short observation time.

The ratio of methyl v. ethyl loss increases from 1:11 to approximately 1:1 (MS 902S, first field free

Table 2. Relative peak areas and kinetic energy releases $(T_{0.5}, \text{ meV})$ for reactions of deuteriated 2-methylpentanes^a

2°metnyi	pentantes							
	CH3(CD3)CHCH2CH2CH3		(CH ₃) ₂ CHCH ₂ CH ₂ CD ₃		(CH ₃) ₂ CHCH ₂ CD ₂ CH ₃		(CH ₃) ₂ CDCH ₂ CH ₂ CH ₃	
Fragment lost	Area	T _{0.5} °	Area	T _{0.5} °	Area	T0.5°	Area	T _{0.5} °
CH3	47 ^b	26	38	25	27	27	27	27
$CH_4(CH_2D)$	33	30	61	31	70	32	73	32
CH ₃ D(CHD ₂ ⁻)	8	29	1		3		_	
$CD_3^{(CH_2D_2)}$	6 ^b	30	—					—
CHD ₃	6	34						_
C₂H₅`	63	21	3]				54	20
C_2H_6	25	20	3		<2	17	39	21
$C_2H_5D(C_2H_3D_2)$	10	21	1 }	20.5 ± 1	62	21	7	20
$C_2H_4D_2(C_2H_2D_3)$	2	22	61		36	21	_	
C ₂ H ₂ D ₂	1	22	32)		—			_

^a Measured on a VG ZAB-2F mass spectrometer, see footnote b in Table 1.

^b The ratio of CH_3 and CD_3 loss is 5:1, the $T_{0.5}$ values are 17 and 23 meV, respectively, when measured on MS 9, see footnote a in Table 1.

° ±3% STD.

region), when the C(2) hydrogen is substituted by deuterium. This is in keeping with tert-pentyl cation formation. A similar observation has been made by Howe for C_3H_7 loss from the next homolog, 2methylhexane, producing tert-butyl cations.¹⁵

2-Methylhexane

The appearance energy of the $[C_6H_{13}]^+$ ions formed by loss of methyl from 2-methylhexane has also been $AE([C_6H_{13}]^+) = 10.64 \pm 0.05 \text{ eV},$ measured. which corresponds to a threshold of 665 kJ mol^{-1} . This is $\Delta H_{\rm f}^{(0)}([sec-hexyl]^+) =$ significantly lower than 723 kJ mol⁻¹ and only 17 kJ mol⁻¹ greater than $\Delta H_{\rm f}^{0}$ $([tert-hexyl]^+)$ (648 kJ mol⁻¹),⁵ which demonstrates that tert-hexyl cations are formed at threshold (timescale $\sim 30 \ \mu$ s, cf. Ref. 3). This may occur in a similar manner as described above for 2-methylpentane; cf. also Ref. 15.

The metastable peak for methyl loss from 2methylhexane has also been measured at both short and long observation times. The peaks were both narrow with $T_{0.5}$ values of 14 (MS 902S) and 17 meV (ZAB-2F), respectively; at long time the peak shape appears to be complex-Gaussian. This indicates that the 2-methylhexane molecular ion retains its structure and mainly produces sec-hexyl cations in the metastable time-frames studied.

CONCLUSIONS

The molecular ion of 2-methylbutane loses methyl without prior rearrangement (no 1,2-methyl shift from C(3) to C(2)) producing sec-butyl cations at threshold;² the molecular ions of pentane and hexane rearrange prior to loss of methyl primarily by a 1,2ethyl shift and to a lesser extent by 1,2-methyl and possible 1,2-propyl shifts.^{2,12,14} These results are compatible with those presented and leads to the general conclusion that the ability of alkyl group migration to initiate dissociation in alkane molecular ions is in the order ethyl>methyl≥propyl. This is also in accord with recent theoretical calculations; it has been found that elongation of the C(2)—C(3) bond in the butane molecular ion (ground state) is favored over elongation of the C(1)--C(2) bond.¹⁶

The present results clearly demonstrate that the combined use of thermochemical measurements and observations of metastable peak shapes in different time-frames may provide considerable insight into the complexity of low energy fragmentation pathways and the structures of the resulting ions; they also demonstrate that structural conclusions based solely on metastable peak measurements do not necessarily correspond to those arrived at on thermochemical grounds.

EXPERIMENTAL

Materials

2-Methylpentane and 2-methylhexane were purchased from Fluka (Puriss.). The deuteriated compounds were prepared by established routes as shown below and redistilled; purity was checked by ¹³C NMR.

$CH_3CH_2CH_2CH(CH_3)COOH \rightarrow \rightarrow$
$\xrightarrow{3}$ CH ₃ CH ₂ CH ₂ CH(CH ₃)CD ₃
$(CH_3)_2CHCH_2CH_2COOH \xrightarrow{1} \xrightarrow{4}$
$\xrightarrow{3}$ (CH ₃) ₂ CHCH ₂ CH ₂ CD ₃
$(CH_3)_2 CHCH_2 COCH_3 \xrightarrow{5} \xrightarrow{4}$
$\xrightarrow{3}$ (CH ₃) ₂ CHCH ₂ CD ₂ CH ₃
$(CH_3)_2C(OH)CH_2CH_2CH_3 \xrightarrow{6}$
$\xrightarrow{3}$ (CH ₃) ₂ CDCH ₂ CH ₂ CH ₃
1: LiA1D ₄ , Ref. 16.
2: HBr/H ₂ SO ₄ , Ref. 18.
3. Bu $Sn\overline{D}$ Ref 10

3: Bu₃SnD, Ref. 19

- 4: $Ph_3P + Br_2/DMF$, Ref. 20.
- 5: LiA1D₄, standard procedure.

6: HBr/LiBr, Ref. 21.

Measurements

Metastable peak shapes for reactions occurring at short times $(1 \ \mu s)$ were measured in the first field free region of a Kratos AEI MS 902S mass spectrometer under good energy resolution by sweeping the acceleration voltage at a constant sector voltage. The main ion-beam width at half-height was 2.5-4 V at an acceleration voltage of 7000 V. The $T_{0.5}$ values were calculated in the usual way and corrected for the main ion beam;⁶ the STD were based on at least five successive scans. The relative abundances of reactions were measured from the metastable peak heights without energy resolution but keeping the acceleration voltage constant for all reactions. They were also measured as peak areas (triangulation) under good energy resolution. The metastable peaks for reactions after long time $(15 \ \mu s)^8$ were measured in the second field free region of a VG ZAB-2F mass spectrometer (MIKE spectra) operating under good energy resolution. The main ion beam at half-height was 2 V at an acceleration voltage of 8000 V. The relative abundances were obtained as peak areas (triangulation).

The appearance energies were measured with energy-selected electrons as described elsewhere.^{3,22}

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