Extrusions of $^{12}CH_3$ and $^{12}CH_4$ from the Molecular Ion of $^{13}CH_3CH_2CH_2{}^{13}CH_3$

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Summary The loss of C-2 (or C-3) as methyl or methane from the butane molecular ion proceeds *via* concerted reactions and does not involve [methylpropane]$^{+\bullet}$ as a reaction intermediate.

THE possible isomerisation of the molecular ion of butane to that of methylpropane prior to decompositions on the μs time-scale and the structures of daughter ions resulting from the loss of H•, CH_3•, and CH_4 from the two hydrocarbons have recently been discussed in detail.[1]

In order to unequivocally identify for [butane]$^{+\bullet}$ the participation of non-terminal C atoms in methyl and methane eliminations therefrom, the ^{13}C-labelled butane, $^{13}CH_3CH_2CH_2{}^{13}CH_3$, was prepared and the metastable peaks for loss of CH_3• and CH_4 and $^{13}CH_3$• and $^{13}CH_4$ were measured; the results are shown in the Table. From these values, assuming that no isotope effect is operating, the proportions of internal and terminal C atom participation were calculated (see Table). It is evident that no appreciable positional loss of identity of C atoms takes place before fragmentation. These results must now be compared with those reported previously[1] for deuterium labelled butanes. The latter data, revised in the form of relative metastable peak areas, are also presented in the Table; each mode of fragmentation will be discussed in turn.

(a) Terminal methyl loss. Examination of the Table shows that terminal methyl loss involves no significant isotope effect.

(b) Terminal methane loss. This, likewise, involves no significant isotope effect when the overall process is considered; for compound (**2**) 39·4%, (**3**) 38·9%, and (**4**) 38·6%. However, the observations permit the reaction to be formally separated into 1,2 + 1,3- and 1,4-eliminations. For (**3**) the 1,2 + 1,3-elimination contributes 14·6% and the 1,4-process, 24·3%. In contrast, for (**4**) the 1,2 + 1,3 contribution is 21·6% and the 1,4 reaction, 17%. These results are compatible with the operation of normal deuterium isotope effects which favour (CH_3–H) over (CH_3–D) and (CD_3–H) over (CD_3–D) for (**3**) and (**4**), respectively.

TABLE. Metastable peak areas[a] for loss of methyl and methane from labelled butanes

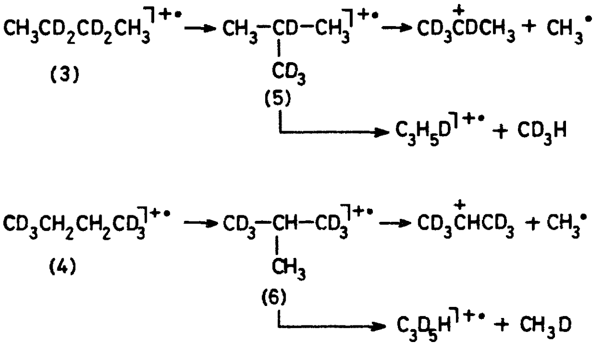
Compound	Fragment lost			
	CH_3•	CH_4	$^{13}CH_3$•	$^{13}CH_4$
$CH_3CH_2CH_2CH_3$ (**1**)	54·8	45·2	—	—
$^{13}CH_3CH_2CH_2{}^{13}CH_3$ (**2**)	4·3	56·3		39·4
		[5·7]	[50·6]	

Compound	CH_3•	CH_4(CH_2D•)	CH_3D(CHD_2•)	CD_3•(CH_2D_2)	CD_3H	CD_4
$CH_3CD_2CD_2CH_3$ (**3**)	51·2	24·3	14·6	3·9	5·7	<0·2
$CD_3CH_2CH_2CD_3$ (**4**)	5·9	<0·5	6·1	48·8	21·6	17·0

[a] Measurements were performed on an AEI GEC MS902S mass spectrometer under conditions of good energy resolution (see J. L. Holmes and J. K. Terlouw, *Canad. J. Chem.*, 1975, **53**, 2076); the electric sector voltage was selected so that all the metastable peaks were measured at the same acceleration potential. Peak areas were measured by planimeter and by weighing; average of 5 values.

(c) Internal methyl loss. The absence of any significant loss of $CH_2D\cdot$ from (**4**), and by inference from the small changes in methyl: methane ratios among the compounds examined that loss of $CHD_2\cdot$ does not contribute to the overall reaction $(\mathbf{3})^{+\cdot} \rightarrow m/z\ 45 + 17$, indicates the participation of only (secondary) methylene H atoms rather than (primary) terminal H atoms in the internal methyl loss.† Some small isotope effect is apparent from the relative losses of $CH_3\cdot$ (4·3%), $CD_3\cdot$ (3·9%), and $CH_3\cdot$ (5·9%) from (**2**), (**3**), and (**4**) respectively, but its origin cannot positively be identified.

(d) Internal methane loss. It appears to be related to internal methyl loss because the relative abundance for loss of $^{12}CH_4$ from (**2**), 5·7%, is similar to that of CD_3H from (**3**), 5·7%, and CH_3D from (**4**), 6·1%.



Many of the above results could readily be explained by invoking partial isomerisation of $[\text{butane}]^{+\cdot}$ to $[\text{methylpropane}]^{+\cdot}$ prior to fragmentation. For example, internal methyl and methane eliminations from (**3**) and (**4**) could be rationalized as in the Scheme. The non-involvement of the tertiary H(D) in the methane elimination has been well established.[2] Although the rationale of the Scheme seems plausible it must be deemed unlikely because metastable ions of (**5**) were found to lose CH_4, CH_3D, and CD_3H in ratios 78 : 18 : <1, *i.e.*, CD_3H loss was a very minor process[1] (with no isotope effect $CH_4 : CD_3H$ would be 1 : 2). Indeed, the participation of methylpropane molecular ions is further rendered unlikely from observations of (**6**). Here loss of CH_3D predominates (91%) with CH_2D_2 (4%), CD_3H (4%), and CD_4 (*ca.* 1%) as minor processes [*cf.* (**4**)].

It is concluded from the above observations that the processes leading to loss of methyl and methane from butane molecular ions (and possibly from alkane ions in general) are best described as concerted and not step-wise reactions, *i.e.*, although the reacting configurations for loss of C-2 (or C-3) as methyl or methane from $[\text{butane}]^{+\cdot}$ may resemble those for the corresponding reactions of $[\text{methylpropane}]^{+\cdot}$ ions, the latter are not involved as discrete reaction intermediates. Observations on ^{13}C labelled hexane, heptane, nonane, and tetradecane have recently been reported by Gäumann *et al.*[3] but the results only described the normal mass spectra of the compounds from which detailed conclusions cannot be drawn.

A typical experimental procedure was as follows. $[1,4\text{-}^{13}C_2]$Butane was prepared by reduction of 1,4-dibromo-$[1,4\text{-}^{13}C_2]$butane[1,4] (90% enriched). 2-Methyl-$[1,1,1,3,3,3\text{-}^{2}H_6]$propane was made as described in ref. 1 using $(CD_3)_2CO$.

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† Note that this closely resembles the preferential insertion in the gas phase of a long-lived carbene into a sec.-C–H bond in propane over insertion into prim.-C–H: H. M. Frey and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, 1957, **79**, 6373.

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[4] A. Murray and D. L. Williams, 'Organic Synthesis with Isotopes,' Interscience, New York, 1958, pp. 129 and 813.