Hydrogen Randomisation Prior to α-Cleavage in 70 ev Mass Spectra of Aliphatic Ketones

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Summary In the 70 ev mass spectra of methyl ketones deuteriated in the α-positions, the loss of CD_3 *via* α-cleavage is accompanied by the loss of CHD_2 and CH_2D; similar loss of CH_3CD_2 from α-deuteriated ethyl ketones is also accompanied by the loss of CH_3CHD and CH_3CH_2.

A RECENT study[1] of deuteriated ketones has shown that at low electron voltages (nominal 10 ev), hydrogen randomisation occurs in the molecular ions prior to fragmentation in the source. Further study[2] showed that randomisation becomes more extensive in ions of lower internal energies and longer lifetimes, such as those decomposing in the first and second field-free regions of a double-focussing mass spectrometer. Nevertheless, in the 70 ev spectra, scrambling is usually absent, or occurs only to a slight extent;[1,2] this is true especially of fragmentation processes involving simple bond cleavages.[2b] It was therefore concluded that the use of the technique of deuterium labelling in general mass spectrometric studies is not precluded, since randomisation occurs extensively only at low voltages. We now present evidence for extensive hydrogen randomisation prior to α-cleavage in the 70 ev spectra of various deuteriated ketones.

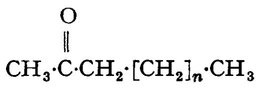
TABLE 1[a]

Peak distributions showing the loss of methyl and deuteriated methyl radicals from penta-deuteriated methyl ketones (II) *at* 70 ev

Compound	M^+-CH_3	M^+-CH_2D	M^+-CHD_2	M^+-CD_3
(II) n = 4	0	2	7	100
5	0	2	7	100
6	0	3	8	100
7	0	5	11	100
8	0	5	13	100
9	3	5	13	100

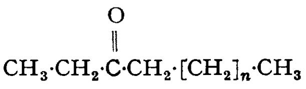
[a] The ion intensities have all been corrected for contributions from natural ^{13}C isotopes and [$^2H_4$]-impurities;[6] the $M^+ - CD_3$ peak is taken as the base peak.

In the 70 ev spectra of tridecan-2-one (I; $n = 9$) the loss of a methyl radical from the molecular ion occurs exclusively *via* an α-cleavage, since there is no corresponding loss of methyl in the spectra of tetradecan-3-one (III; $n = 9$). In the 70 ev spectra of 1,1,1,3,3-[$^2H_5$]tridecan-2-one (II; $n = 9$), the loss of 18 mass units (CD_3) from the molecular ion is accompanied by the loss of 17, 16, and 15 mass units (CHD_2, CH_2D, and CH_3, respectively). The abundance of the intensities of the $M^+ - 17$, $M^+ - 16$, and $M^+ - 15$ daughter peaks (Table 1) shows clearly that at 70 ev, hydrogen randomisation is by no means negligible, even for ions undergoing simple bond cleavages.



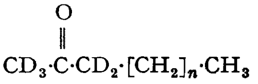
$CH_3\cdot\overset{O}{\overset{\|}{C}}\cdot CH_2\cdot[CH_2]_n\cdot CH_3$

(I)



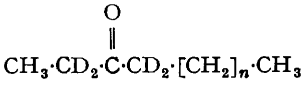
$CH_3\cdot CH_2\cdot\overset{O}{\overset{\|}{C}}\cdot CH_2\cdot[CH_2]_n\cdot CH_3$

(III)



$CD_3\cdot\overset{O}{\overset{\|}{C}}\cdot CD_2\cdot[CH_2]_n\cdot CH_3$

(II)



$CH_3\cdot CD_2\cdot\overset{O}{\overset{\|}{C}}\cdot CD_2\cdot[CH_2]_n\cdot CH_3$

(IV)

Similar evidence for hydrogen randomisation is observed in the spectra of other penta-deuteriated methyl ketones (II; $n = 4$—8). It is noteworthy that there is a small but distinct increase in the extent of randomisation with increase in chain length of the ketones. The addition of an extra methylene group (three atoms) results in an increase of nine vibrational degrees of freedom in the molecular ion, into which the internal energy (transferred by initial electron impact) may be distributed. This "degree of

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freedom effect"[3,4] leads to an increase in the average lifetimes of the ions, and hence to greater scrambling prior to fragmentation. Furthermore, the addition of methylene groups increases the number of hydrogens on the longer alkyl chain available for hydrogen/deuterium interchange, thus increasing the scrambling.

The loss of CH_3CHD and CH_3CH_2‡ in addition to the loss of CH_3CD_2 from both 2,2,4,4-[$^2H_4$]tridecan-3-one and 2,2,4,4-[$^2H_4$]tetradecan-3-one (IV; $n = 8$ and 9, respectively) at 70 ev, is also extensive in contrast to 2,2,4,4-[$^2H_4$]octan-3-one and 2,2,4,4-[$^2H_4$]hepan-3-one (IV; $n = 3$ and 2, respectively). Indeed, the hydrogen/deuterium interchange is even greater in the ethyl ketones than in the corresponding methyl ketones. This difference is consistent with the general mass spectrometric observation that the transfer of secondary hydrogens is more favoured than the corresponding transfer of primary hydrogens.[5] As with the methyl ketones, an increase in chain length also increases the extent of scrambling in the ethyl ketones (Table 2).

Slight increases in the average lifetimes of the ions (obtained by variation of the accelerating voltage and repeller potential) increase significantly the extent of scrambling in the ions.[7] Very extensive scrambling is observed in the metastable transitions in the second field-free region [*e.g.* $M^+ - CH_3CD_2$: $M^+ - CH_3CHD$; $M^+ - CH_3CH_2$ is 20:52:28 for 2,2,4,4-[$^2H_4$]tridecan-3-one (IV; $n = 8$)]. This is in accord with previous observations.[2]

The present unequivocal evidence for extensive hydrogen randomisation in 70 ev spectra, preceding reactions generally accepted as involving simple single bond cleavages, has serious implications for the interpretation of deuterium labelling studies of relatively large organic compounds. In such compounds, ions of relatively long lifetimes probably play an important role in determining the 70 ev spectra; hydrogen/deuterium interchange must therefore be allowed for in the interpretation of deuterium labelling data.

TABLE 2[a]

Peak distributions showing the loss of ethyl and deuteriated ethyl radicals from tetra-deuteriated ethyl ketones (IV) *at* 70 ev

Compound	$M^+ - CH_3CH_2$	$M^+ - CH_3CHD$	$M^+ - CH_3CD_2$
(IV) $n =$ 2	0	0	100
3	0	6	100
8	8	29	100
9	12	33	100

[a] The ion intensities have all been corrected for contributions from natural ^{13}C isotopes and [$^2H_3$]-impurities;[6] the $M^+ - CH_3CD_2$ peak is taken as the base peak.

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‡ The loss of CH_3CD_2, CH_3CHD and CH_3CH_2 must come from an α-cleavage process, because there is no loss of an ethyl radical in the corresponding spectra of the methyl ketones.

[1] W. A. Carpenter, A. M. Duffield, and C. Djerassi, *J. Amer. Chem. Soc.*, 1968, **90**, 160.

[2] (a) A. N. H. Yeo, R. G. Cooks, and D. H. Williams, *Chem. Comm.*, 1968, 1269; (b) A. N. H. Yeo and D. H. Williams, *J. Amer. Chem. Soc.*, 1969, **91**, 3582.

[3] R. G. Cooks and D. H. Williams, *Chem. Comm.*, 1968, 627.

[4] F. W. McLafferty and W. T. Pike, *J. Amer. Chem. Soc.*, 1967, **89**, 5951.

[5] See for example, H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, 1967, p. 157.

[6] A. N. H. Yeo, following communication.

[7] A. N. H. Yeo, unpublished data.