A General Method for Deriving the Mass Spectra of Fully Deuteriated Compounds from the Spectra of their Partially Deuteriated Analogues

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Summary The mass spectra of fully deuteriated compounds can be calculated from the spectra of two of their partially deuteriated analogues of different isotopic purities.

THE use of deuteriated compounds for mechanistic studies in organic mass spectrometry is well-known.[1] However, it is usually difficult to prepare deuteriated compounds of very high isotopic purity (>95%) for such studies. The presence of isotopic impurity impedes the quantitative interpretation of the results from the daughter-ion peaks, particularly if hydrogen scrambling is implicated. We now report the use of a simple procedure by which the spectra of *fully* deuteriated compounds can be derived from the spectra of two *partially* deuteriated analogues with different isotopic purities; this procedure has been applied to an investigation of hydrogen scrambling in molecular ions of some deuteriated ketones undergoing α-cleavages.[2]

The Table illustrates the procedure for the calculation of the loss of CH_3CD_2,CH_3CHD, and CH_3CH_2 radicals from the molecular ions of 2,2,4,4-[$^2H_4$]tridecan-3-one at 70 ev. Each group of peaks in the observed spectra is (i) corrected for the presence of natural ^{13}C isotopes; and (ii) normalised to 100 for convenience of comparison. Two sets of data are so treated, and the data are then "solved simultaneously" to cancel out the peaks due to the [$^2H_3$]-impurities.

The calculated data in (7) (Table) compare well with the

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most highly deuteriated ketone (**8**) (96%, [$^2H_4$]; 4%, [$^2H_3$]), obtained after six successive base-catalysed exchanges with an excess of deuterium oxide.[3] The observed data in (**3**), (**4**), and (**8**) clearly indicate the approach towards the calculated data with increased deuteriation. Further checks using separately the combinations of the data in (3) and (8), and the data in (4) and (8), give the same results as in (7), showing that the method is self-consistent.

Only one assumption is made in the calculations—the positional distribution of the deuteriums in the partially deuteriated analogues (with different isotopic purities) is assumed to be the same. For example, in the compound considered, the distribution of the unexchanged hydrogen in the α-positions of the two side-chains (in 20% [$^2H_3$]-ketone and 8% [$^2H_3$]ketone) is the same in both analogues. In general, this condition will hold if the deuteriated analogues are prepared by the same method.

The calculation of peak intensities of daughter ions $M^+-CH_3CD_2$, M^+-CH_3CHD, and $M^+-CH_3CH_2$ in the *mass spectra of* 2,2,4,4-[$^2H_4$]-*tridecan*-3-*one at* 70 ev

	Molecular ions		Daughter ions			
	[$^2H_4$]	[$^2H_3$]	$M^+ - 29$	$M^+ - 30$	$M^+ - 31$	$M^+ - 32$
m/e	202	201	173	172	171	170
(1)[a]	100	24	10	36	100	9
(2)[b]	96·6	24	7·1	24·0	98·9	9
(3)[c]	80·0	20·0	5·1	17·2	71·2	6·5
(4)[d]	92·0	8·0	5·6	19·5	72·3	2·6
(5)[e]	230·0	20·0	14·0	48·7	180·8	6·5
(6)[f]	150·0	—	8·9	31·5	109·6	—
(7)[g]	100	—	6	21	73	—
(8)[h]	96	4	6	20	73	1

[a] Observed spectra; the largest peak in each group is taken as the base peak. [b] Data in (**1**) corrected for carbon-13 isotope contribution. [c] Total intensity in each group in (**2**) normalised to 100. [d] Steps b and c applied to another set of data from second partially deuteriated analogue. [e] Data in (**4**) multiplied by the factor 20/8 to cancel out contribution from *m/e* 201. [f] Data in (**3**) subtracted from data in (**5**). [g] Data in (**6**) normalised to 100 for each group (*i.e.* division by 150/100). [h] Data for a third partially deuteriated analogue after steps b and c given for comparison with calculated data in (**7**).

This general method can be adapted for compounds with poorer isotopic purities (*e.g.* [$^2H_4$]-ketones contaminated with [$^2H_3$]- and [$^2H_2$]-analogues). In such cases, three sets of data of partially deuteriated analogues are required before the data can be solved to give the spectra of the fully deuteriated compounds.

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[1] See for example, H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, 1967; J. H. Beynon, R. A. Saunders, and A. E. Williams, "The Mass Spectra of Organic Molecules," Elsevier, Amsterdam, 1968.

[2] A. N. H. Yeo, preceding communication.

[3] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Structural Elucidation of Natural Products by Mass Spectrometry," Vol. 1, Holden-Day, San Francisco, 1964, p. 19.