Evidence for Intra- and Inter-alkyl Hydrogen–Hydrogen Exchange in the Mass Spectra of Ethyl Acetate

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Summary Electron-impact induced randomisation of hydrogens in the molecular ions of ethyl acetate occurs *via* at least two different and distinct mechanisms, one scrambling only the ethyl hydrogens, and the other scrambling the acetyl and ethyl hydrogens in the molecular ions.

IN connection with a study on the mechanisms for the loss of water from molecular ions of compounds with the formula R–CO–Y, the loss of water from the molecular ion of ethyl acetate was studied in detail, with the aid of deuterium labelling.

The loss of water from the molecular ion of ethyl acetate has a low activation energy, as is shown by the presence of a large metastable peak (>20 times the size of the next largest metastable in the spectrum). Deuterium labelling in the acetyl positions of the molecular ions (Ib) shows conclusively that the two hydrogens come *exclusively* from the ethyl positions, for daughter ion formation in the source (Table). Labelling in the methylene positions of the ethyl group (Ic) and (Id) shows that the loss of water in the source involves the loss of H_2O, HDO, and D_2O (Table). If it is assumed that there is no scrambling of the hydrogens, these results would require at least three different competing pathways for the loss of water, accounting for the loss of (i) two methyl hydrogens, (ii) one methyl hydrogen and one methylene hydrogen, and (iii) two methylene hydrogens, in the ratios of about 39 : 52 : 9. It is extremely unlikely that this is so, since the same rationalisation would require at least six different competing pathways of very similar activation energies for loss of water, to account for the decompositions in the first and second field-free regions of a double focussing mass spectrometer.

$$CR^1_3CO_2CR^2_2CR^3_3$$

(I)

	R^1	R^2	R^3
a;	H	H	H
b;	D	H	H
c;	H	D	H
d;	D	D	H

Allowing for hydrogen randomisation,† the results of all the deuteriated esters can be easily accounted for in terms

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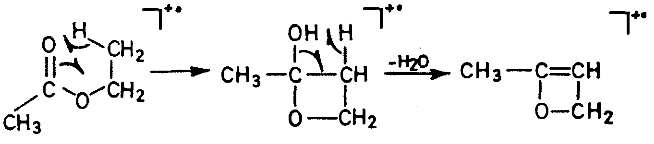
† The loss of C_2H_3 (27 mass units) from the molecular ion of ethyl acetate also occurs after extensive hydrogen scrambling of the ethyl hydrogens.[1,2]

of a decomposition pathway such as that shown in Scheme 1.‡



SCHEME 1

The loss of water from the molecular ions of ethyl acetate[a]

	Compound	$M^{+}-H_2O$	$M^{+}-HDO$	$M^{+}-D_2O$
(Ia)	Daughter ion (70ev)	100	0	0
	$^{1}m^{*}$(70ev)[b]	100	0	0
	$^{2}m^{*}$(70ev)[b]	100	0	0
(Ib)	Calc.(ER)[c]	100	0	0
	Daughter ion	100	0	0
	$^{1}m^{*}$	78	20	2
	$^{2}m^{*}$	59	35	6
	Calc.(CR)[d]	35·7	53·6	10·7
(Ic)	Calc. (ER)	30·0	60·0	10·0
	Daughter ion	39	53	8
	$^{1}m^{*}$	41	51	8
	$^{2}m^{*}$	47	47	6
	Calc. (CR)	53·6	42·9	3·6
(Id)	Calc. (ER)	30·0	60·0	10·0
	Daughter ion	39	52	9
	$^{1}m^{*}$	24	62	14
	$^{2}m^{*}$	17	58	25
	Calc. (CR)	10·7	53·6	35·7

[a] The total intensity for water loss has been normalised to 100 in all the compounds; all the data refer to 70 ev spectra.

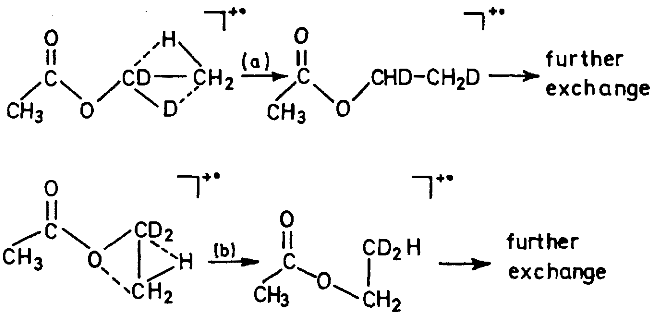
[b] $^{1}m^{*}$ and $^{2}m^{*}$ refer to the intensities of the metastable transitions in the first and second field-free regions of an AEI MS9 mass spectrometer.

[c] Calculated ratios for Complete Randomisation of only the Ethyl hydrogens, assuming no isotope effects.

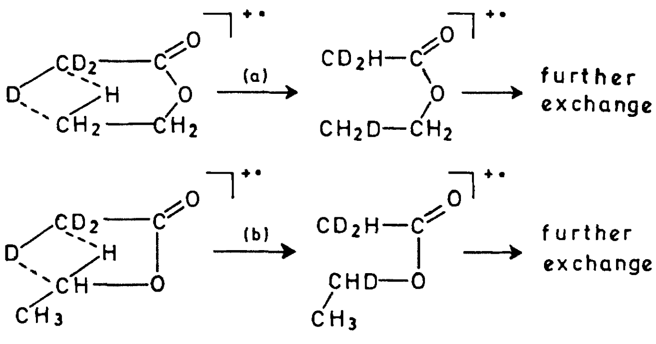
[d] Calculated ratios for Complete Randomisation of all the hydrogens in the molecular ions, assuming no isotope effects.

For decomposition in the source, only the hydrogens in the ethyl group are scrambled prior to water loss (Table). If it is assumed that no isotope effects operate, the results show almost complete randomisation of the five ethyl hydrogens prior to water loss (Table). Two mechanisms for this randomisation are possible (Scheme 2a and 2b[2]), each going through a four-membered transition state. It is not possible, at the moment, to say conclusively which of the two mechanisms operate, but each can independently account for the scrambling, which is confined only to the ethyl hydrogens (intra-alkyl hydrogen randomisation). The results suggest that at 70 ev, the average rate for the loss of water from the molecular ion is greater than that for inter-alkyl hydrogen randomisation, but slower than that for intra-alkyl hydrogen randomisation.

For ions with lower internal energies (and hence longer lifetimes), such as those decomposing in the first and second field-free regions of the mass spectrometer, inter-alkyl hydrogen scrambling is observed (Table); *i.e.* acetyl hydrogens interchange with the ethyl hydrogens. This interchange can take place *via* either a six-membered transition state (Scheme 3a) or a five-membered transition state (Scheme 3b). Either of these schemes, in conjunction with Scheme 2a or 2b can account for the results of loss of water in all the deuteriated esters in the field-free regions. Scrambling is more extensive (approaching complete randomisation, assuming no isotope effects) in ions undergoing metastable transitions in the second field-free region than those in the first field-free region; this increase in the extent of hydrogen scrambling with increase in the lifetime of the molecular ions sampled, is in accord with previous observations.[5] Intra- and inter-alkyl hydrogen randomisation is also observed in the mass spectra of ethyl propionate.[6]



SCHEME 2



SCHEME 3

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‡ Ionised cyclobutanols (analogous to the postulated ionised oxacyclobutanol) have been shown to be intermediates in the decomposition of aliphatic aldehydes.[3,4]

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[6] A. N. H. Yeo, unpublished results.