Base-initiated Reformatsky Condensations in the Gas Phase

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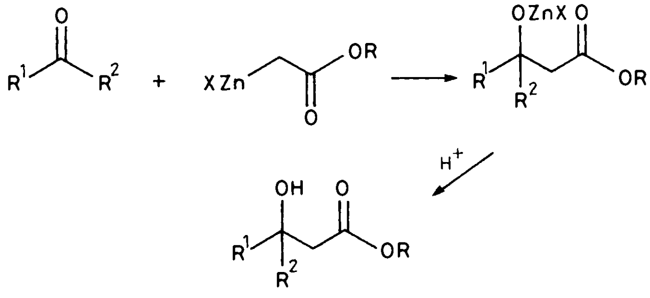
The ester enolate anion $CH_2{=}C(OEt)O^-$ reacts with acetaldehyde and with acetone in the gas phase to produce 'stable' adducts that are amenable to study by collisional activation and tandem mass spectrometry (MS/MS). The activated adducts and deprotonated β-hydroxy ethyl ester reference ions both decompose by elimination of H_2O, $Et^•$, H_2O followed by EtOH, and by a retro reaction to reform $CH_2{=}C(OEt)O^-$. The losses of H_2O, $Et^•$, and EtOH are assigned to be characteristic of a species of tetrahedral geometry. These losses are, however, attenuated for the ion–molecule adducts because, in addition to existing as tetrahedral complexes, they are also formed as ion–dipole and proton-bound species.

The study of gas-phase negative ion–molecule reactions has become a significant area of research in gas-phase ion chemistry. In particular, considerable attention has been focused on reactions such as nucleophilic substitution and addition at carbonyl centres.[1–5] With the development of experimental techniques such as the Fourier transform ion-cyclotron resonance (FT-ICR),[6–8] flowing afterglow (FA),[9] chemical ionization (CI),[10] and high pressure mass spectrometry,[11] important discoveries have been made in the understanding of gas-phase negative ion reactions.[12]

Specifically, the aforementioned techniques make it possible to study the intrinsic properties of adducts formed between nucleophilic negative ions (*e.g.* RO^-, F^-, NH_2^-) and neutral substrates (*e.g.* those that contain $>C{=}O$, ArH, –CN) without the complications of solvent effects. The absence of solvent in an ion–molecule reaction, conducted in the gas phase, can result in an altered rate of reaction. For example, the reaction $Cl^- + MeBr \longrightarrow Br^- + MeCl$ occurs 10^{12} times faster in the gas phase than in dimethylformamide as the solvent. This is because activation energies for gas-phase reactions are lower than the corresponding activation energies for reactions carried out in solution. Indeed, a number of gas-phase reactions occur at the collision frequency.[12]

For those nucleophilic substitution reactions that do not proceed at the collision frequency, loosely associated complexes were proposed as intermediates, and a tetrahedral species is actually the transition state.[3] Loosely associated species such as ion–dipole complexes are appropriate because the nucleophile and substrate are freely rotating species, whereas a covalent adduct is formed after the energy of rotation is converted into vibrational energy. Thus, there is a decrease in the number of quantum-mechanical degrees of freedom. Although the forward reaction may be lower in energy than the reverse reaction, the reverse reaction may be entropically favoured. This is the so-called entropy bottleneck.

Many gas-phase nucleophilic addition reactions were carried out in FT-ICR cells at low pressures (*e.g.* 10^{-6}–10^{-7} Torr*) in which there is a low probability for stabilization of an adduct through a third-body collision. Thus, an adduct produced with considerable exothermicity has little chance of surviving detection (*i.e.* lifetimes are greater than 1 ms) without some other means of efficient stabilization (*e.g.* radiative emission). Nevertheless, considerable information concerning reaction rates (efficiencies) and fragmentation processes are obtained from FT-ICR studies.



Scheme 1.

A nucleophilic addition adduct formed with excess energy under conditions of higher pressure (*e.g.* FA and CI) is often collisionally stabilized by either a buffer gas (FA) and/or unreactive neutrals. The coupling of CI with tandem mass spectrometry enables the structures of these stable adducts to be determined by collisional activation decomposition CAD mass spectrometry.[13]

Using this approach, we previously investigated the gas-phase base-initiated aldol condensation.[4] The enolate anions $CH_2{=}CHO^-$ and $CH_2{=}CMeO^-$ react with acetaldehyde and acetone to produce 'stable' adducts, which were studied by collisional activation and tandem mass spectrometry (MS/MS). Differences in the relative abundances of characteristic losses from the gas-phase adducts compared to appropriate model compounds point to the existence of at least three adducts; *viz.* ion–dipole, proton-bound, and tetrahedral complexes. The major constituents are loosely-associated ion–dipole and proton-bound complexes.

In this paper, we report on the gas-phase Reformatsky reaction. The condensed-phase reaction was first discovered in 1866 by Reformatsky.[14] The generally accepted mechanism is illustrated in Scheme 1. In the presence of zinc, an α-halo ester condenses with an aldehyde or ketone to form a β-hydroxy ester. Ethyl acetate enolate anion reacts with acetone and with acetaldehyde. The following questions arise: (*i*) are structurally similar adducts formed as those previously described for the aldol condensations? (*ii*) Specifically, are the stable adducts loosely associated species (*e.g.* ion–dipole or proton-bound) or of tetrahedral geometry? We also compare the CA mass spectra of these adducts with those of appropriate model compounds. The structures of the condensation products are then discussed on the basis of these comparisons.

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* 1 Torr = 133.32 Pa.

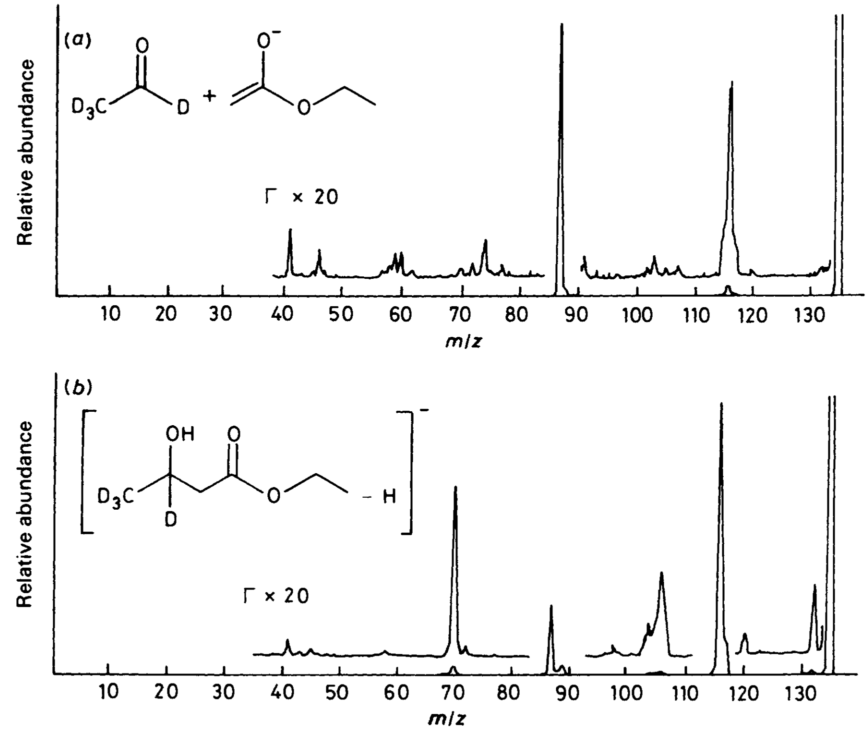
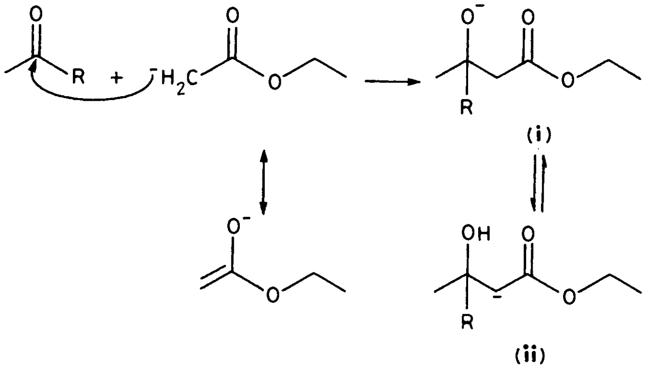
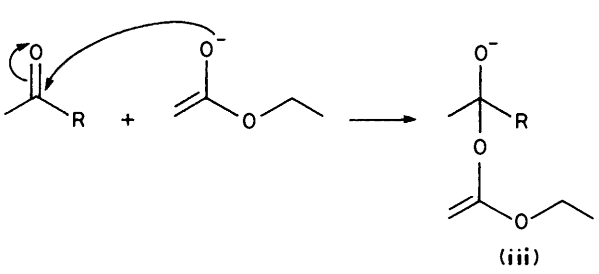


Figure. CA mass spectrum of (*a*) the adduct formed in the reaction of ethyl acetate enolate ion with [$^2H_4$]acetaldehyde and (*b*) the $(M - H)^-$ ion of ethyl 3,4,4,4[$^2H_4$]butanoate (**1**).

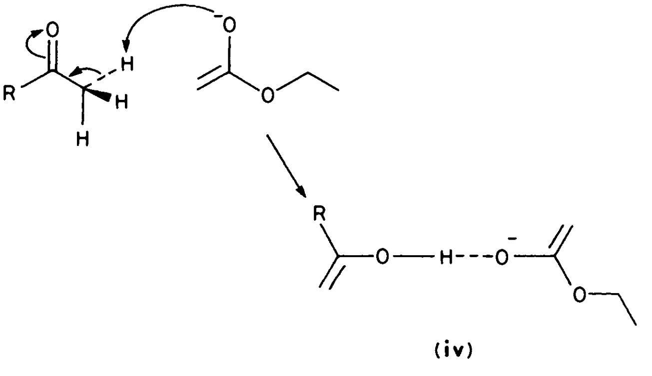


Scheme 2.

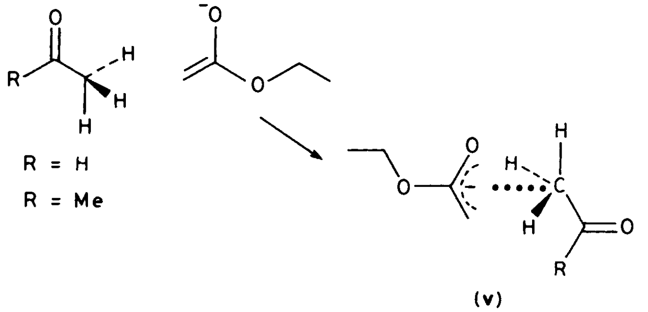


Scheme 3.

Enolate negative ions are readily produced by deprotonation of alkyl carbonyl compounds by using EtO^- (formed by the dissociative secondary-electron capture of ethyl nitrite[15–17]) in a chemical-ionization (CI) source. It was shown that collisionally activated decompositions of enolate ions are structurally specific.[18] 'Isolation' of the adduct can be achieved by mass selection in a tandem mass spectrometer, which permits the investigation of the intrinsic properties of the reaction adduct.



Scheme 4.



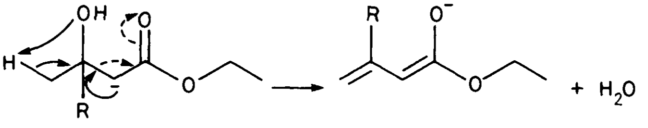
Scheme 5.

Results and Discussion

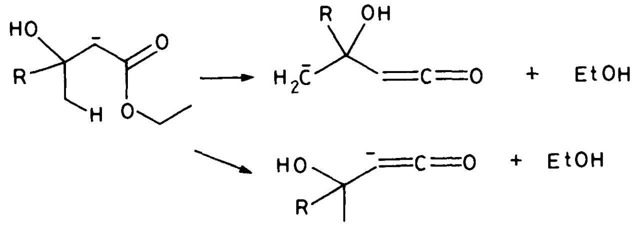
The collisional activation (CA) mass spectrum of an adduct $C_6D_4H_7O_3^-$ (*m/z* 135) formed in the reaction of ethyl acetate enolate negative ion with [$^2H_4$]acetaldehyde [Figure (*a*)] shows that the major fragmentation of the adduct is the loss of C_2D_4O to give rise to an ion of *m/z* 87. Minor losses of D$^•$, D_2, HDO, H_2O, D_2O, EtOH, $C_4DH_7O_2$, and $C_4D_4H_6O_2$, and an

Table 1. CA mass spectra of adducts from reaction of ethyl acetate enolate anion with acetaldehyde, and with acetone.

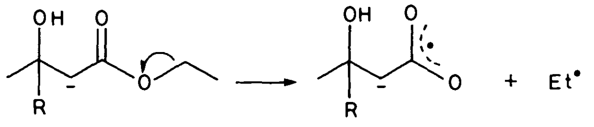
Neutral	Loss (% abundance)									
	H•	H_2	Me•	H_2O	Et•	EtOH	reversion/retro	H_2O and EtOH	$MeCO_2Et$	m/z 41
MeCHO	<1	<1	<1	3	<1	<1	90	<1	5	1
CD_3CDO	<1	<1	<1	3	<1	1	93	<1	<1	<1
Me_2CO	<1	—	<1	13	<1	<1	82	1	<1	1
$(CD_3)_2CO$	<1	—	<1	<1	<1	<1	93	1	2	<1



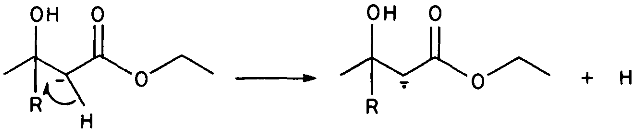
Scheme 6.



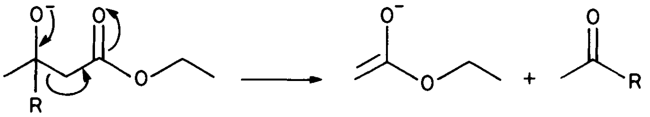
Scheme 7.



Scheme 8.



Scheme 9.



Scheme 10.

apparent consecutive loss of HDO and EtOH are also observed. The loss of C_2D_4O can occur from an adduct formed by a Reformatsky condensation (Schemes 2 and 3) or from loosely associated species (Schemes 4 and 5). The minor losses are indicative of a covalently bound adduct (**i**) as shown in Schemes 6–10. The loss of H_2O and D_2O is presumably the result of scrambling through ene–ol tautomerization involving (**i**) and (**ii**), respectively (Scheme 2).

The CA mass spectra of adducts formed in reactions of ethyl acetate enolate anions and acetaldehyde or acetone (Table 1) show that analogous fragmentation behaviour pertains to these adducts. Specifically, the major fragment ion in each system is formed by reversion to the alkyl acetate enolate ion. Charge reversal (CR)[19,*] of the ion of m/z 87, produced by CA of the adduct formed between ethyl acetate enolate and acetone in an MS/MS/MS experiment, gave a mass spectrum of ions that is identical with the CR spectrum of ethyl acetate enolate ion.

The CA mass spectrum [Figure (*b*)] of the $(M - H)^-$ ion of the model compound (**1**) (see Table 2), (*i.e.*, the Reformatsky condensed-phase product) shows a major loss of HD, HDO, and minor losses of Et•, EtOH, C_2D_4O, $C_4D_4H_6O_2$, and consecutive losses of HDO and EtOH. That the losses of HDO with EtOH are consecutive was determined in an MS/MS/MS experiment: the $(M - HDO)^-$ ion upon subsequent collisional activation eliminates predominantly EtOH. The fragmentation behaviour is analogous to that described for alkyl acetoacetate ions.[20]

The CA mass spectra of the $(M - H)^-$ ions of other Reformatsky model compounds [*i.e.* (**2**), (**3**), (**4**), Table 2] are directly comparable to the $(M - H)^-$ ion of (**1**). The major fragmentation in all cases is the loss of water. A number of minor losses are also observed; *viz*., the losses of H•, H_2 [for models (**2**), and (**5**)–(**7**)], Et•, EtOH, MeCHO [for models (**2**), (**5**), and (**6**)], Me_2CO [for models (**3**) and (**7**)] and a consecutive loss of H_2O and EtOH. These fragmentations are analogous with those already described for (**1**); thus, it is likely that the fragmentations occur by the same mechanism in each case (Schemes 6–10).

A Reformatsky product must initially have the charge located on the oxygen (see Scheme 2). Upon deprotonation of the model compounds (**1**)–(**4**) two possible $(M - H)^-$ ions may be generated: one by the abstraction of an α-proton (**ii**) or another by removal of an hydroxy proton (**i**). Thus, there is uncertainty with respect to the initial location of the charge, although interconversion of the two species is certainly possible. To estimate the composition of the mixture that forms with the charge initially centred on oxygen, we have turned to the model compounds ethyl 3-trimethylsiloxy butanoate (**5**) [2,2-$^2H_2$]-3-hydroxybutanoate (**6**), and ethyl [2,2-$^2H_2$]-3-hydroxy-3-methylbutanoate (**7**) because these species can be generated with the charge initially centred on oxygen.

The reaction of (**5**) with EtO^- generates an adduct that loses TMSOEt to form an $(M + EtO^- - TMSOEt)^-$ ion with the charge initially centred on the oxygen[21] (Scheme 11). This species is the expected Reformatsky intermediate (see Scheme 2). Upon CA, this species primarily fragments by loss of water. Minor fragment ions formed by loss of H•, H_2, C_2H_5•, C_2H_4O, EtOH, $C_4H_8O_2$, $C_4H_9O_2$, and H_2O followed by EtOH are also observed (see Table 2).

The CAD spectra of the $(M - H)^-$ ions of the model compounds (**1**) and (**2**) agree qualitatively with that of (**5**). The major difference is that the ion produced from (**5**) gives a higher relative abundance of the ion of m/z 87, which is formed by a retro reaction (Scheme 9), than do the $(M - H)^-$ ions of (**1**) and (**2**). The differences may be due to the location of charge on oxygen for (**5**), whereas (**1**) and (**2**) are a mixture of alkoxide ion and carbanion [*i.e.* structures (**i**) and (**ii**)]. Another possible

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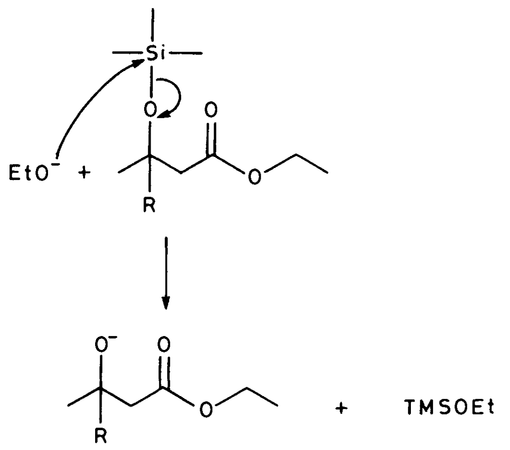
[*] Collision of a negative ion with a collision gas (*e.g.* He) can effect charge stripping leading to a decomposing positive ion. This produces a charge reversal mass spectrum. If two negative ions give identical charge reversal mass spectra, there is a probability that the original negative ions have the same structure.

Table 2. CA mass spectra of $(M - H)^-$ ions of ethyl β-hydroxyesters.

Model compound	Loss (% abundance)									
	$H^•$	H_2	$Me^•$	H_2O	$Et^•$	EtOH	reversion/ retro	H_2O and EtOH	$MeCO_2Et$	m/z 41
(1) $CD_3CD(OH)CH_2CO_2Et$	<1	<1	<1	74	1	3	17	2	<1	<1
(2) $MeCH(OH)CH_2CO_2Et$	<1	<1	<1	73	<1	2	18	3	<1	<1
(3) $Me_2C(OH)CH_2CO_2Et$	<1	—	<1	77	<1	4	11	6	<1	<1
(4) $(CD_3)_2C(OH)CH_2CO_2Et$	<1	—	<1	73	<1	5	16	5	<1	<1
(5) $MeCH(OTMS)CH_2CO_2Et$[a]	<1	<1	<1	60	<1	1	33	2	<1	<1
(6) $MeCH(OH)CD_2CO_2Et$	<1	<1	<1	87	<1	6	1	<1	<1	<1
(7) $Me_2C(OH)CD_2CO_2Et$	<1	<1	<1	82	<1	3	6	7	<1	<1

[a] Reference ion is $[MeCH(OTMS)CH_2CO_2Et + EtO^- - EtOTMS]^-$.



Scheme 11.

reason for the difference is that the species formed between **(5)** and EtO^- loses neutral TMSOEt, and this removes energy which drives enolization.

Moreover, there are also those ions formed that are representative of a species fragmenting as a carbanion [*i.e.* structure **(ii)**]. For example, the loss of water must come from an ion in which the charge is centred on carbon (*cf.* Scheme 6). Thus, some interconversion takes place on the mass spectrometry time scale.

The model compounds **(6)** and **(7)** can also be used to generate, specifically, a species with the charge initially centred on oxygen. Upon CA, the $(M - H)^-$ ion, which has the charge centred initially on oxygen, fragments by expelling $H^•$, H_2/HD for **(6)**, H_2O, HDO, D_2O, $Et^•$, $MeCHO/Me_2CO$, EtOH, EtOD, HDO followed by EtOH (see Table 2). The major fragmentation in each case is the loss of HDO, a process that is consistent with the results only if isomerization takes place prior to fragmentation (see Scheme 6).

The CAD spectra of each adduct reveal that the major fragmentation process is reversion to the alkyl acetate enolate ion, whereas the model compounds give most abundant ions by losing water. This is the clearest evidence that more than one structure is being produced in the ion–molecule reactions.*

The CAD spectrum of a mixture of isomeric structures will be composite. The composition of the mixture can be calculated by using linear combinations of reference spectra provided all appropriate reference spectra are available. By using the loss of water as a representative fragmentation of a tetrahedral structure [*i.e.* the equilibrium mixture of structures **(i)** and **(ii)**], we calculate that only a small fraction of the adduct exists as a tetrahedral species (1.3% for the $[^2H_4]$acetaldehyde/ethyl acetate system).

A proton-bound complex [structure **(iv)**] of the ethyl acetate enolate ion/$[^2H_4]$acetaldehyde system, would fragment upon CA to give a mixture of both the enolate ions of ethyl acetate and acetaldehyde. Using the ratio of the acetaldehyde to ethyl acetate enolate ions generated by the $(M - H)^-$ ion of **(1)** as a reference point and comparing it with that ratio found for the adduct, we are able to ascertain that the adduct generates more acetaldehyde enolate ion (m/z 46) than does **(1)**.

By knowing the relative acidities of A^- and B^-, the way in which a proton-bound species decomposes to partition itself between A^- and B^- should be predictable.[22] Those measurements for methyl acetate, acetaldehyde, and acetone reveal that it requires 19.7 and 11.3 kJ more energy to remove a proton from acetaldehyde and acetone, respectively, than from methyl acetate.[23] Collisional activation adds more than enough energy to overcome a barrier of 19.7 kJ; therefore, upon CA a proton-bound dimer of ethyl acetate and acetaldehyde should fragment to a mixture of the ethyl acetate and acetaldehyde enolate ions. However, the ethyl acetate anion will predominate because it has a lower proton affinity than that of the acetaldehyde enolate ion. Thus, some fraction of the adduct exists as a proton-bound complex.

The other contributor to the ion–molecule adduct is an ion–dipole complex [structure **(v)**]. Upon CA, loosely associated complexes of this type revert back to the starting material. The adducts produce very large abundances of the alkyl enolate ion (m/z 87) with respect to the rest of the fragment ions; this is in accord with the conclusion that some portion of the adduct exists as an ion–dipole complex.

Conclusions

In conclusion, the adducts of the Reformatsky reactions and the corresponding reference ions undergo fragmentations in a characteristic and novel manner upon collisional activation. Species of tetrahedral geometry are formed in small amounts in the gas-phase, base-initiated Reformatsky reaction between ethyl acetate enolate ions and carbonyl compounds. The majority of the adducts exist as loosely associated complexes (*i.e.* proton-bound and ion–dipole). These results are similar to those previously reported for the gas-phase, base-initiated aldol reaction.[4] For the aldol reaction, however, the tetrahedral adduct is formed in much lower abundance under the time and pressure constraints of a high pressure source.

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* It is conceivable that only the loosely associated complexes are formed in the ion source, and that upon collisional activation these isomerize to give the covalent adduct. The residence time of an ion in the collision cell under our experimental conditions is, however, only 10^{-7} s. It is unlikely, therefore, that both processes of isomerization and of fragmentation can occur during this time span.

Experimental

Mass Spectrometry.—CAD mass spectra were measured with a Kratos MS-50 triple analyser mass spectrometer,[24] which consists of a Nier–Johnson geometry high-resolution mass spectrometer followed by an electrostatic analyser (ESA-II). An ion of interest formed in the source was selected at a mass resolution of 3 000–5 000 (10% valley) by using MS-1 (ESA-I and the magnetic sector). ESA-II was scanned to give the CAD spectrum of the mass-selected ion. In a typical CAD experiment, 5–10 scans were acquired and signal-averaged. Ion–molecule reactions were performed in a commercially available (Kratos Scientific Instruments Mark IV) chemical-ionization source: temperature 100 °C, accelerating voltage 8 kV. Liquids were introduced through a commercially available (Kratos Scientific Instruments) reagent gas inlet system or through a custom-fabricated all-glass heated inlet system operated at 100 °C. Carbanions were generated by H^+/D^+ abstraction by EtO^-. The EtO^- was generated from ethyl nitrite by dissociative secondary electron (at 70 eV) resonance capture.[15–17] The indicated source housing pressure of ethyl nitrite was typically 1×10^{-6} Torr. The pressure of each substituent was typically 2×10^{-5} Torr, giving a combined estimated source pressure of approximately 0.1 Torr. The pressure of helium in the second field-free region cell was sufficient to give a 50% beam suppression.

Reference Compounds.—The alkyl β-hydroxy esters ethyl [3,4,4,4-$^{2}H_{4}$]-3-hydroxybutanoate (**1**), ethyl 3-hydroxy butanoate (**2**), ethyl [3,4,4,4-$^{2}H_{4}$]-3-hydroxy-3-methylbutanoate (**3**), and ethyl 3-hydroxy-3-methylbutanoate (**6**) were prepared from the ethyl bromoacetate and acetaldehyde, or acetone, by the following general method.[25]

A suspension of the appropriate carbonyl compound (5 mmol), ethyl bromoacetate (6 mmol), zinc dust (9 mmol), iodine (1 mmol) in anhydrous dioxane (10 cm^3) was sonicated for 0.5 h. The reaction mixture was poured into an ice–water mixture (100 cm^3), dichloromethane added (100 cm^3), and the two phases separated. The organic phase was washed with water (2×50 cm^3), dried ($MgSO_4$), and excess solvent removed at 15 °C *in vacuo* (15 mmHg). Distillation of the residue gave the corresponding β-hydroxy ester in (on average) 90% overall yield.

Ethyl 3-*trimethylsiloxybutanoate* (**5**). 1,1,1,3,3,3-Hexamethyldisilizane (3.23 g, 20 mmol) was added drop-wise to a stirred mixture of (**1**) (2.64 g, 20 mmol) and anhydrous pyridine (1.58 g, 20 mmol) at 20 °C over a period of 5 min and then stirred at 20 °C for 4 h. Water (10 cm^3) was added, the product extracted into ether (2×10 cm^3), the organic phase separated and washed with water (10 cm^3), dried over anhydrous $MgSO_4$ and distilled to yield ethyl 3-trimethylsiloxybutanoate in high yield.[26]

Ethyl [2,2-$^{2}H_{2}$]-3-*hydroxybutanoate* (**6**) *and Ethyl* [2,2-$^{2}H_{2}$]-3-*hydroxy*-3-*methylbutanoate* (**7**). These compounds were prepared by treating (**2**) and (**4**), separately in 1 mol dm^{-3} NaOD (tenfold excess) at 20 °C for 30 min.

Acknowledgements

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References

1 G. Klass and J. H. Bowie, *Aust. J. Chem.*, 1980, **33**, 2271; G. Klass, D. J. Underwood, and J. H. Bowie, *ibid.*, 1981, **34**, 507; J. C. Sheldon, *ibid.*, 1981, **34**, 1189; G. Klass, J. C. Sheldon, and J. H. Bowie, *ibid.*, 1982, **35**, 2471; J. C. Sheldon and J. H. Bowie, *ibid.*, 1983, **36**, 289.

2 J. E. Bartmess, R. L. Hays, and G. Caldwell, *J. Am. Chem. Soc.*, 1981, **103**, 1338.

3 J. I. Brauman, W. N. Olmstead, and C. A. Lieder, *J. Am. Chem. Soc.*, 1975, **97**, 6685; W. E. Farneth and J. I. Brauman, *ibid.*, 1976, **98**, 5546; W. N. Olmstead and J. I. Brauman, *ibid.*, 1979, **101**, 3715; M. J. Pellerite and J. I. Brauman, *ibid.*, 1980, **102**, 5993.

4 R. N. Hayes, R. P. Grese, and M. L. Gross, *J. Am. Chem. Soc.*, 1989, **111**, 8336.

5 I. H. Williams, G. M. Maggiora, and R. L. Schowen, *J. Am. Chem. Soc.*, 1980, **102**, 6619, 7832.

6 M. B. Comisarow, in 'Transform Techniques in Chemistry,' ed. P. R. Griffiths, Plenum Press, New York, 1978, ch. 10, p. 257.

7 A. G. Marshall, *Acc. Chem. Res.*, 1985, **18**, 316; M. L. Gross and D. L. Rempel, *Science*, 1984, **226**, 261.

8 N. M. M. Nibbering, *Recl. Trav. Chim. Pays-Bas*, 1981, **100**, 297; N. M. M. Nibbering, *Nachr. Chem. Tech. Lab.*, 1984, **32**, 1044; N. M. M. Nibbering, *Adv. Mass Spectrom.*, 1985, **10**, 417; N. M. M. Nibbering, in 'Specialist Periodical Reports: Mass Spectrometry,' ed. M. E. Rose, The Royal Society of Chemistry, London, 1985, vol. 8, p. 141.

9 C. H. DePuy and V. H. Bierbaum, *Acc. Chem. Res.*, 1981, **14**, 146; C. H. DePuy, J. J. Grabowski, and V. M. Bierbaum, *Science*, 1987, **218**, 955.

10 A. G. Harrison, 'Chemical Ionization Mass Spectrometry,' CRC Press, Boca Raton, Florida, 1983.

11 P. Kebarle, *Ann. Rev. Phys. Chem.*, 1977, **28**, 445.

12 J. H. Bowie, *Mass. Spectrom. Rev.*, 1984, **3**, 8.

13 K. Levsen and F. W. McLafferty, *J. Am. Chem. Soc.*, 1974, **96**, 139; C. C. Van de Sande and F. W. McLafferty, *ibid.*, 1975, **97**, 4613; B. Van de Graaf, P. P. Dymerski, and F. W. McLafferty, *J. Chem. Soc., Chem. Commun.*, 1975, 918.

14 S. N. Reformatsky, *Ber. Bunsenges. Phys. Chem.*, 1887, **20**, 1210; 1895, **28**, 2463, 2842.

15 K. Jaeger and A. Henglein, *Z. Naturforsch., Teil A*, 1967, **22**, 700.

16 R. T. McIver and J. S. Miller, *J. Am. Chem. Soc.*, 1974, **96**, 4323.

17 D. P. Ridge and J. L. Beauchamp, *J. Am. Chem. Soc.*, 1974, **96**, 3595.

18 J. H. Bowie, M. B. Stringer, R. N. Hayes, M. J. Raferty, G. J. Currie, and P. C. H. Eichinger, *Spectrosc. Int.*, 1985, **4**, 277.

19 J. H. Bowie, and T. Blumenthal, *J. Am. Chem. Soc.*, 1975, **97**, 2959; I. Howe, J. H. Bowie, J. E. Szulejo, and J. H. Beynon, *Int. J. Mass Spectrom. Ion Phys.*, 1980, **34**, 99.

20 P. C. H. Eichinger and J. H. Bowie, *Org. Mass Spectrom.*, 1987, **22**, 103.

21 V. C. Trenerry, J. C. Sheldon, and J. H. Bowie, *Aust. J. Chem.*, 1981, **34**, 519.

22 S. A. McLuckey, D. Cameron, and R. G. Cooks, *J. Am. Chem. Soc.*, 1981, **103**, 1313.

23 J. E. Bartmess, J. A. Scott, and R. T. McIver, Jr., *J. Am. Chem. Soc.*, 1979, **101**, 6046.

24 M. L. Gross, E. K. Chess, P. A. Lyon, F. W. Crow, S. Evans, and H. Tudge, *Int. J. Mass Spectrom. Ion Phys.*, 1982, **42**, 243.

25 B. H. Han and P. Boudjouk, *J. Org. Chem.*, 1982, **47**, 5031.

26 H. C. Carter and R. C. Ganer, *J. Lipid Res.*, 1967, **8**, 391.

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