The Unimolecular Dissociation of $(CH_3)_2C^{\oplus}CH_2COOH$ in the Gas Phase: An Acid-Ester Type Rearrangement Involving the Formation of the Proton-Bound Acetone-Ketene Ion $[(CH_3)_2C=O\cdots H\cdots CH_2=C=O]^{\oplus}$ **

Ben L.M. van Baar, Johan K. Terlouw*,
Semiha Akkök, Waltraud Zummack, Thomas Weiske, and Helmut Schwarz*

Abstract: In the gas phase the β-ketocarbenium ion $(CH_3)_2C^{\oplus}CH_2COOH$ is proposed to rearrange to the proton-bound acetone-ketene ion $[(CH_3)_2CO\cdots H\cdots CH_2CO]^{\oplus}$, prior to its dissociation into $CH_3CO^{\oplus}/(CH_3)_2CO$ and $(CH_3)_2COH^{\oplus}/CH_2CO$. Collision experiments in a mass spectrometer of reversed geometry on ^2H- and ^{13}C-labeled isotopomers indicate that this remarkable rearrangement is characterized by two consecutive [1,5]-proton migrations rather than a direct [1,3]-hydrogen shift.

While there exists ample experimental evidence for the [1,2]-migration of a $C(OH)_2^{\oplus}$ group towards a vicinal *radical* centre[1] examples of analogous Wagner-Meerwein type shifts of electron withdrawing groups to *carbenium* ion centres are quite uncommon[2]. A notable example for such a process has been reported by *Berner* et al.[3]. On dissolution in HSO_3F/SO_2ClF at $-100\,°C$, the doubly ^{13}C-labeled acid **1** upon warming to $0\,°C$ rearranges via intermediates **2** and **3** to the acid **4** (Scheme 1). Based on the analysis of the carbon-carbon coupling constants the alternative pathway **2**→**6** (Scheme 1), which would involve consecutive migrations of a CH_3, phenyl (Ph), and CH_3 group, respectively, was ruled out. The preference of CO_2H over CH_3 group migration was attributed to a stability difference between the cationic intermediates **3** and **5**, the latter as an α-ketocarbenium ion being less stable than the tertiary carbenium ion **3**.

We report here on a novel rearrangement of a β-ketocarbenium ion in the gas phase, the central stages of which involve the intermediate generation of ion-dipole complexes and proton-bound dimers[4]. It is further proposed that in the formation of these complexes the intramolecular [1,3]-hydrogen shift does not compete with two consecutive [1,5]-proton migrations[5].
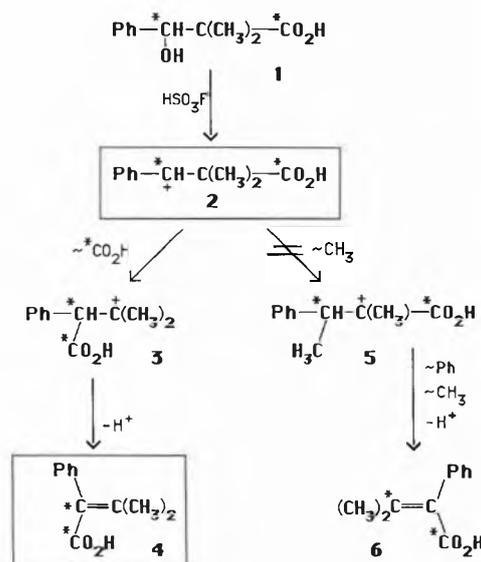
Electron impact (70 eV) ionization of *tert*-butylacetic acid (**7**) generates, among other species $[M - CH_3]^{\oplus}$ ions at m/z 101 (7% of the base peak at m/z 57, $C_4H_9^{\oplus}$). The study of the labeled analogues **7a–7d** (see Table 1) proves that the methyl loss is a specific process (absence of any hydrogen scrambling) involving exclusively the *intact tert*-butyl group. The reaction is approximately thermoneutral[6] but it does not occur among the metastable molecular ions. This indicates that it is a fast direct bond cleavage process confined to the ion source yielding product ions having initially the structure of the β-ketocarbenium ion **8** (Scheme 2).
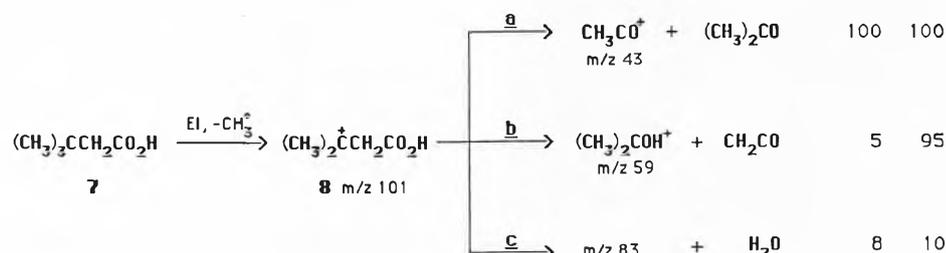
The stability of this tertiary cation may be enhanced by homoconjugative interaction of the carbenium ion centre with the $C=O$ group, as demonstrated earlier by *Vogel* for many other systems[8]. The mass-selected m/z 101 ion shows three major unimolecular dissociations (Scheme 2) in its metastable ion (MI) and collisional activation (CA) mass spectra. Based on analyses of the CA mass spectra of the product ions it was concluded that the m/z 43 ion is the acetylium ion, $CH_3CO^{\oplus}$, whereas m/z 59 is protonated acetone. The C_3H_6O neutral co-generated in the process m/z 101 → m/z 43 is exclusively *acetone* as evidenced by the close resemblance of its CIDI[9] spectrum [m/z 58 (100%), 43 (65%), 42 (13%), with O_2 for ionization] with the NRMS[9] spectrum of acetone, using Xe for neutralization and O_2 for reionization.

From these observations it is obvious that the products can neither be generated directly from **8** nor from any other intermediate analogous to the rearrangement **2**→**3**, in Scheme 1; rather it is

Scheme 1

Scheme 2

			Relative abundance (% base-peak)	
			MI	CA
$(CH_3)_3CCH_2CO_2H$ **7**	$\xrightarrow{EI, -CH_3^{\cdot}}$ $(CH_3)_3\overset{+}{C}CH_2CO_2H$ **8** m/z 101	$\xrightarrow{a}$ CH_3CO^+ + $(CH_3)_2CO$ m/z 43	100	100
		$\xrightarrow{b}$ $(CH_3)_2COH^+$ + CH_2CO m/z 59	5	95
		$\xrightarrow{c}$ m/z 83 + H_2O	8	10

tempting to propose that m/z 101 prior to its unimolecular dissociations **a** and **b** (see Scheme 2) rearranges to a proton-bound complex of acetone and ketene (**9**). By using the relationship of *Larson* and *McMahon*[12] and the enthalpies of formation of $(CH_3)_2CO$ ($\Delta H_f^0 = -217$ kJ/mol[13]) and CH_2CO ($\Delta H_f^0 = -48$ kJ/mol[13]) the estimated enthalpy of formation of **9**, 316 kJ/mol, is comparable in energy to that of the «starting» ion **8**. From the proton-bound complex **9**, both $CH_3CO^{\oplus}/(H_3C)_2CO$ (reaction channel **a**) and $(H_3C)_2COH^{\oplus}/CH_2CO$ (reaction channel **b**) can be directly generated. Reaction channel **a** is favoured over the competing process **b** by 23 kJ/mol[14] assuming that the formation of **9** from either product combination involves no energy barrier. As shown earlier by *Cooks* et al.[16] such a small enthalpy difference may account for the observation that the proton-bound complex **9** predominantly yields $CH_3CO^{\oplus}/(H_3C)_2CO$ in its MI spectrum; upon collisional activation the two reaction channels **a** and **b** become largely equivalent.

Does **8** indeed rearrange to the proton-bound dimer **9** and if so, how? Before addressing this important question it should be noted that ionized *tert*-butylacetate, $CH_3CO_2C(CH_3)_3$ **10**, in a nearly thermoneutral[17] reaction, also undergoes loss of a methyl radical; the latter originates exclusively from the *tert*-butyl group, since $CD_3CO_2C(CH_3)_3$ loses no $CD_3^{\ominus}$. If the so formed ion m/z 101 is subjected to a MS/MS experiment its properties with regard to processes **a** and **b** appear to be the same as those of the m/z 101 ion generated from **7**. In particular the shape of the metastable ion peak for reaction channel **a** (generation of $CH_3CO^{\oplus}/(H_3C)_2CO$) and the derived kinetic energy release, $T_{0.5} = 5$ meV, are identical for both precursors. Such a small $T_{0.5}$ value is characteristic[4, 16] for the dissociation of proton-bound species, but it does not necessarily prove the intermediacy of such species. Notable differences (the origin of which will be discussed below) in the unimolecular and collision-induced dissociations of the m/z 101 ion generated from **10** are the absence of H_2O loss (reaction channel **c**) and the presence of m/z 58 ions in the CA spectrum. The latter ion was identified as ionized acetone.

We conclude that the initially generated ions **8** (from **7**) and **11** (from **10**) both communicate, presumably via the proton-bound complex **9**, prior to their dissociation into $CH_3CO^{\oplus}$ (m/z 43) + $(CH_3)_2CO$ and $(CH_3)_2COH^{\oplus}$ (m/z 59) + CH_2CO.

To obtain more insight in the unimolecular isomerization processes the labeled analogues of **7** and **10**, shown in Table 1, were studied.

Before interpreting the labeling results presented in Table 1 in terms of a mechanism for the common dissociation pathways **a** and **b** from the acid **7** and the ester **10** it is instructive to first turn to the

H_2O loss from m/z 101 which is unique to the acid.

The MI spectra of mass-selected $[M - CH_3]^{\oplus}$ ions generated from **7b**, **7c**, and **7d** (not shown), indicate that specific positions are involved in the formation of H_2O from **8**. We observe in the spectrum of **7b** that the H/D atoms of the α-methylene group do not contribute to the loss of water. $[M - CH_3]^{\oplus}$ ions generated from **7d** (i.e. deuterated in the carboxy group) and **7c** (i.e. deuterated in the *t*-butyl group) on the other hand show losses of H_2O and HDO in the ratio 4:1 and H_2O, HDO, D_2O in the ratio 8:10:1, respectively. Hence there is an extensive exchange between the hydroxy and methyl hydrogen atoms. In fact these results can be interpreted in terms of a complete equilibration among the methyl and hydroxy hydrogen atoms with a kinetic isotope effect of 1.8 ± 0.2. We propose that the equilibrations $8 \rightleftharpoons 8'$ via a [1,5]-proton exchange precedes the actual proton transfer to the OH group ($\rightarrow 8''$). From the latter, H_2O is easily[20] eliminated to generate the product ion $[CH_2=C(CH_3)-CH_2-C=O]^{\oplus}$ (Scheme 3).

Scheme 3
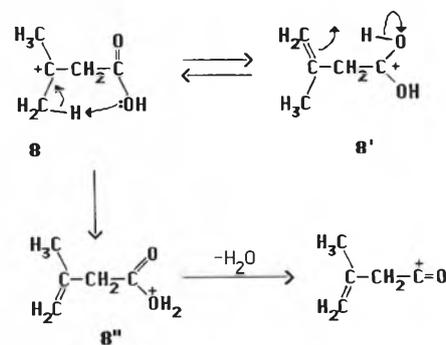
The labeling results shown in Table 1 can be summarized as follows:

1) The carboxy carbon atom is fully retained in the acylium ion $CH_3CO^{\oplus}$ (mass shift m/z 43 → m/z 44 in the MI spectrum

of **7a**). Protonated acetone does not contain the original carboxy carbon atom.

2) From the study of **7b** it is obvious that the α-methylene group serves as building block for $CH_3CO^{\oplus}$ (mass shift m/z 43 → m/z 44). As shown in Table 1, the methylene deuterium also participates in the formation of protonated acetone (m/z 59 vs. m/z 60). The deuterium atom is exclusively contained in the hydroxy group of the ion, since the CIDI spectrum exclusively yields signals of unlabeled acetone.

3) The third hydrogen atom of the acylium ion is provided by one of the methyl groups of the original *tert*-butyl functionality. The $[M - CH_3]^{\oplus}$ ion generated from **7c** nicely demonstrates that both the CH_3 and the CD_3 group participate with nearly equal probabilities. In the formation of protonated acetone the methyl groups are largely retained (base peak m/z 62). However, the CIDI spectra of the corresponding *neutral* acetone molecules $C_3H_3D_3O$ (m/z 61) and $C_3H_4D_2O$ (m/z 60) show the following intensity distribution in the structure-characteristic m/z 46 to m/z 42 region: 46 (6%), 45 (70%), 44 (100%), 43 (40%), and 42 (25%). This indicates that the majority of the neutral acetone molecules are not CD_3COCH_3 and CD_2HCOCH_3 (which would yield prominent ions at m/z 46 and m/z 45) but rather CD_2HCOCH_2D and CDH_2COCHD_2. These results are easily explained if prior to dissociation an extensive exchange occurs among the methyl hydrogen atoms via the equilibration $8 \rightleftharpoons 8'$ proposed in Schema 3.

4) The MI and CA spectra of **7d** show that the hydrogen atom of the carboxy group is only partially incorporated in the acetyl cation. The resulting m/z 44 $CH_2D-C=O^{\oplus}$ ions most likely come from the hydrogen exchange reaction $8 \rightleftharpoons 8'$ proposed above and not from a direct [1,3]-hydrogen transfer of the hydroxylic hydrogen to the α-methylene moiety. A confirmation that the neutral C_3H_5DO formed in the reaction m/z 102 → m/z 43 is labeled

Table 1. Label distribution for the unimolecular dissociations of mass-selected $[M - CH_3]^{\oplus}$ ions generated from **7**, **10** and their isotopomers[a].

Neutral Precursor		Relative Abundance[b]								
		m/z 43 MI	m/z 43 CA	m/z 44 MI	m/z 44 CA	m/z 58 CA	m/z 59 CA	m/z 60 CA	m/z 61 CA	m/z 62 CA
$(CH_3)_3CH_2CO_2H$	(**7**)	100	100	–	–	–	95	–	–	–
$(CH_3)_3CH_2{}^{13}CO_2H$	(**7a**)	–	–	100	100	–	95	–	–	–
$(CH_3)_3CHDCO_2H$	(**7b**)	–	10	100	100	–	80	20	–	–
$(CH_3)_2CD_3CH_2CO_2H$ (**7c**)[c]		100	55	94	50	–	–	–	11	100
$(CH_3)_3CH_2CO_2D$	(**7d**)	100	73	22	19	–	–	100	–	–
$CH_3CO_2C(CH_3)_3$	(**10**)	100	100	–	–	5	35	–	–	–
$CD_3CO_2C(CH_3)_3$	(**10**)	100	100	–	–	–	5	35	–	–

[a] Mass spectra were recorded on the VG ZAB-2F (in Utrecht) and VG ZAB-HF-3F (in Berlin) mass spectrometers. The former is of BE configuration and the latter of BEB configuration (B denotes magnetic and E electric sector). A full description of the two machines is given in Ref.[19]. Briefly, $[M - CH_3]^{\oplus}$ ions generated by 70 eV electron impact ionization in the ion source are accelerated to 8 keV kinetic energy, mass selected by means of B, and the metastable ion (MI) and collisional activation (CA, collision gas: helium) spectra recorded by scanning of E. All compounds were synthesized by standard laboratory procedures, purified by gas chromatography, and characterized by spectroscopic means.

[b] Relative abundances are given in % base peak. Note that irrespective of the precursor used no signals at m/z 45 and m/z 46 were recorded (see text for discussion).

[c] From **7c** upon 70 eV electron impact ionization both $CH_3^{\ominus}$ and $CD_3^{\ominus}$ are eliminated in a ratio of 2:1. In the present context only the data of the mass-selected m/z 104 $[M - CH_3]^{\oplus}$ are of interest.

acetone $CH_3C(O)CH_2D$ and not its enol is evidenced by its CIDI spectrum (losses of CH_3° and CH_2D° in a 1:1 ratio). If the neutral would have corresponded to the enol form, due to a nonergodic behaviour[21], a markedly different ratio is expected[21].

A feasible mechanism which is in keeping with all experimental findings is given in Scheme 4[22]. We first note that all intermediates depicted in this scheme are thermochemically accessible; their enthalpies of formation are well below the energy required for the exit channels a and b. Once 12 is formed ring opening to 13 is feasible, and the fate of the latter species is mechanistically quite intriguing. The «shortest» path would involve the direct enol-ketonization step 13→11 via [1,3]-hydrogen migration. If this reaction were to occur, the original carboxy group should be fully retained in the $CH_3CO^\oplus$ fragment and should act as protonating species in the generation of protonated acetone. The data in Table 1 and the arguments described above are not in line with these requirements. Obviously the energy-demanding direct [1,3]-hydrogen migration[23] cannot compete with two successive [1,5]-«proton» migrations[5]. In the first one, 13→14, an «acidified» hydrogen of the methyl group is transferred intramolecularly to the terminal carbon atom of the C=C double bond; the latter acts as an intramolecular base. A further [1,5]-proton migration 14→11 follows; in this step the original proton of the carboxy group (whose acidity must be significantly increased due to the presence of the positive charge at the carbon atom) is transferred to the C=C double bond. Because of the extensive H/D exchange 8⇌8', the data presented in Table 1 cannot be used to establish unequivocally

whether the reaction sequence 13→14→11 is reversible or irreversible. However, the analysis suggests that the forward reaction 13→14→11 is favoured over the reverse process. This is supported by the fact that the ions generated from 7 lose H_2O whereas those generated from 10 do not; thus 8 is able to rearrange to 11 but not vice versa. Ion 11 serves as the actual precursor for the proton-bound complex 9. The labeling data for 11 (generated from 10a) provide evidence that at this stage no further hydrogen exchange processes occur. This may well reflect the fact that the process 11→9 is energetically more favoured than the reaction sequence 11→14→13. Further support for this conclusion is derived from the study of 11 generated from acetone under the condition of chemical ionization. In fact, from acetone one can generate 11 (presumably via the ion-molecule reaction of $CH_3CO^\oplus$ – generated by α-cleavage of $CH_3C(O)CH_3^{\oplus\circ}$ – with neutral $CH_3C(O)CH_3$); the CA spectrum of this mass-selected m/z 101 ion is indeed very similar to the CA spectrum of 11 generated from 10 (m/z 43, 100%; m/z 58, 4%; m/z 59, 20%; and *no* loss of H_2O). If one uses perdeuterated acetone as a precursor, the analogous m/z 110 ion gives rise to m/z **46** ($CD_3CO^\oplus$) and m/z **66** (($CD_3)_2COD^\oplus$).

The generation of ions 11 from 7, 10 and the above ion-molecule reaction in acetone satisfactorily accounts for the description of the major dissociation pathway of the metastable ions, i.e. the formation of $CH_3CO^\oplus + CH_3C(O)CH_3$, but it does not immediately explain the formation of m/z 59, protonated acetone, in the CA mass spectrum. This observation can, however, readily be explained if an interconversion between ions 11 and the pro-

ton-bound dimer 9 would be possible well below the dissociation limit. The formation of such a proton-bound ion from 11 may be triggered by the expected low energy requirement for the lengthening of the oxygen-to-carbonyl bond (due to hyperconjugative interaction of the CO group with the carbenium centre[8], since this leads to a stable ion-dipole complex of an acetone molecule and an acetyl cation, 11' (Scheme 4). As a result the expected high energy barrier[21] for a [1,3]-hydrogen shift in the covalently bound species may become much lower. The formation of an ion-dipole complex of an acetone molecule and an acetyl cation is favoured by the large dipole moment of acetone, 2.88 ± 0.02 D (water: 1.85 ± 0.02 D). Ab initio calculations on the [vinyl alcohol/water]$^{\oplus\circ}$ system[24] and the [ketene/water]$^{\oplus\circ}$ system[25] have shown that ion-dipole complexes between ionized vinyl alcohol and a water dipole (which has a smaller dipole moment than acetone) have stabilization energies of ca. 60 kJ/mol towards dissociation and that they can easily interconvert with $C\cdots H\cdots O$-bridged ions such as $[H_2O\cdots H\cdots C(H)=CHOH]^{\oplus\circ}$. Such $C\cdots H\cdots OH_2$-bridged species have a relatively short C-H bond (typically 1.08 Å) and a much longer $H\text{-}OH_2$ bond (typically 1.84 Å), and the C-H hydrogen atom does not exchange with the hydrogen atoms of the $\cdots OH_2$ moiety. By analogy with this system it seems likely that at internal energies well below the dissociation limit of 11 the fraction of the m/z 101 ions 11 having sufficient internal energy interconvert with the proton-bound structure 9 as depicted in Scheme 4.

Our proposal involves that the initial «oxygen» transfer occurs via 8→12 and not via a [1,3]-hydroxyl migration[26]

Scheme 4
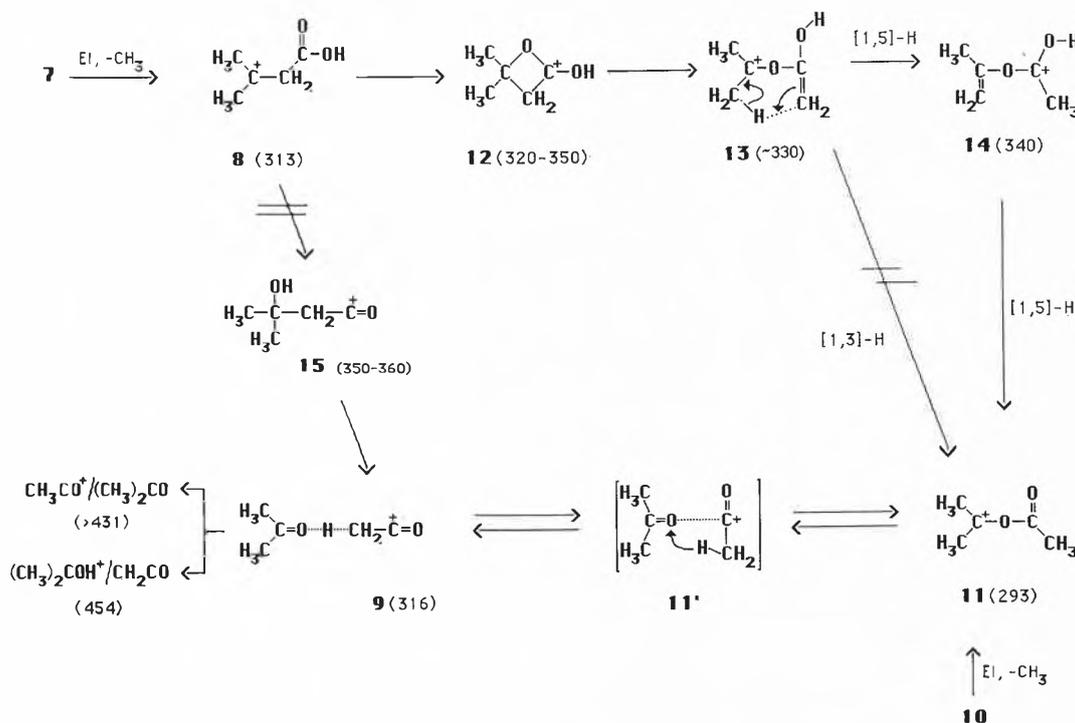
$8 \rightarrow 15 \rightarrow 9$. This pathway cannot immediately be rejected on the basis of the labeling experiments because of the extensive H/D exchange between the hydroxy and methyl hydrogen atoms. However, we feel it is unlikely to compete with our proposed pathway for the following reasons: (a) the isomerization step $8 \rightarrow 15$ involves the ether-protonated β-isovalerolactone as an intermediate which is considerably higher in energy than the carbonyl-protonated lactone 12; (b) the isomerization step $15 \rightarrow 9$ requires a [1,3]-H shift, the energy demand of which, in contrast to the step $11 \rightarrow 9$, is not lowered by ion-dipole stabilization. One could also argue that the step $15 \rightarrow 9$ involves a [1,5]-H transfer to the carbonyl oxygen with concomitant cleavage of the $C(OH)–C(H_2)$ bond, yielding the proton-bound ion $[(CH_3)_2C=O \cdots H \cdots O=C=CH_2]^{\oplus}$. This ion is only expected to yield $(CH_3)_2COH^{\oplus} + CH_2CO$ in its MI spectrum since the energy requirement for $CH_2=COH^{\oplus} + (CH_3)_2CO$ exceeds that for the first process by 158 kJ/mol[27].

Finally it is of interest to note that the β-ketocarbenium ion 8 and the protonated lactone ion 12 (Scheme 4) have also been generated in solution: upon hydrolysis β-isovalerolactone yields $(CH_3)_2C(OH)CH_2COOH$, via ring opening of 12 by an $A_{Al}1$ mechanism to give 8, followed by the addition of H_2O [28].

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[5] For many examples of [1,n]-*hydride* migrations to carbenium centres see Ref.[2].

[6] $\Delta H_f^0[(CH_3)_3C\text{-}CH_2COOH^{\oplus \ominus}] = 448$ kJ/mol[7a], $\Delta H_f^0[^{\ominus}CH_3] = 142$ kJ/mol[7b], $\Delta H_f^0[(CH_3)_2C^{\oplus}\text{-}CH_2COOH, 8] = 313$ kJ/mol. The heat of formation of 8 has been estimated using: $\Delta H_f^0[(CH_3)_2C^{\oplus}\text{-}CH_2CH_3] = 673$ kJ/mol[7c], $\Delta H_f^0[(CH_3)_2CH\text{-}CH_2CH_3] = -155$ kJ/mol[7d], $\Delta H_f^0[(CH_3)_2CH\text{-}CH_2COOH] = -515$ kJ/mol[7d].

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[8] See Ref.[2], chapter 7.9.

[9] CIDI = Collision Induced Dissociative Ionization[10]; NRMS = Neutralization Reionization Mass Spectrometry[11].

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[14] $\Delta H_f^0[CH_3CO^{\oplus}] = 648$ kJ/mol[15a], $\Delta H_f^0[(CH_3)_2CO] = -217$ kJ/mol[13], $\Delta H_f^0[(CH_3)_2COH^{\oplus}] = 502$ kJ/mol[15b], $\Delta H_f^0[CH_2CO] = -48$ kJ/mol[13]; note that the energy difference between process a and b gets smaller if $\Delta H_f^0[CH_3CO^{\oplus}] = 657$ kJ/mol is used, based on *PA* $[CH_2CO]$[13].

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[17] $\Delta H_f^0[(CH_3)_3C\text{-}OC(O)CH_3^{\oplus \ominus}] = 430$ kJ/mol, estimated from $\Delta H_f^0[(CH_3)_3C\text{-}OC(O)CH_3, 10] = -525$ kJ/mol[18a] and *IE*[10] = 9.9 eV[18b]; $\Delta H_f^0[CH_3CO_2C^{\oplus}(CH_3)_2, 11] = 293$ kJ/mol, estimated, using $\Delta H_f^0[(CH_3)_2CH\text{-}OH] = -272$ kJ/mol[7d], $\Delta H_f^0[(CH_3)_2CH\text{-}OC(O)CH_3] = -481$ kJ/mol[7d], and $\Delta H_f^0[(CH_3)_2C^{\oplus}\text{-}OH] = 502$ kJ/mol[15b]; hence $\Delta H_f^0[11] + \Delta H_f^0[^{\ominus}CH_3] = 435$ kJ/mol.

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[20] For the generation and characterization of hydroxy-protonated acids, $RC(O)OH_2^{\oplus}$, analogues to 17, see: C. G. De Koster, J. K. Terlouw, K. Levsen, H. Halim, H. Schwarz, *Int. J. Mass Spectrom. Ion Proc. 61* (1984) 87.

[21] See Ref.[4o] and many references cited therein.

[22] Heats of formation of the species, given in parentheses in kJ/mol, if not already referred to, were estimated using the following data: $\Delta H_f^0[12]$ was obtained from $\Delta H_f^0[\beta,\beta\text{-dimethyl-}\beta\text{-propiolactone}] = -362$ kJ/mol, by additivity[18a] and from proton affinities (*PA*) of small organic acids and esters (*PA* of lactones are unknown). *PA* of small organic acids and esters are in the range of 820–850 kJ/mol[13]; hence $\Delta H_f^0[12] = 320$–350 kJ/mol. Ion 13 differs from 11 in that the *neutral* keto moiety is replaced by the thermodynamically less favourable *neutral* enol moiety[23]. Thus $\Delta H_f^0[13]$ is expected to be higher than $\Delta H_f^0[11]$ by ≈ 40 kJ/mol, the enthalpy difference between CH_3CHO and $H_2C=CHOH$ (J. L. Holmes, F. P. Lossing, *J. Am. Chem. Soc. 104* (1982) 2648); $\Delta H_f^0[14] = 340$ kJ/mol was estimated using the following data: $\Delta H_f^0[H_2C=C(CH_3)\text{-}OC(O)CH_3] = -351$ kJ/mol[7d], $PA[H_2C=C(CH_3)\text{-}OC(O)CH_3] \approx PA[(CH_3)_2CH\text{-}OC(O)CH_3] = 839$ kJ/mol[13]; $\Delta H_f^0[15]$ was estimated as 350–360 kJ/mol from $\Delta H_f^0[CH_3CH_2CO^{\oplus}]$ and applying the technique and graph in Ref.[15b].

[23] For many examples and further references see: N. Heinrich, W. Koch, G. Frenking, H. Schwarz, *J. Am. Chem. Soc. 108* (1986) 593.

[24] R. Postma, S. P. van Helden, J. H. van Lenthe, P. J. A. Ruttink, J. K. Terlouw, J. L. Holmes, *Org. Mass Spectrom. 23* (1988), in press.

[25] R. Postma, P. J. A. Ruttink, J. K. Terlouw, J. L. Holmes, *J. Chem. Soc. Chem. Commun.* (1986) 683.

[26] Examples on [1,3]-OH migration are reported in: B. Ciommer, H. Schwarz, *Z. Naturforsch. B 34* (1979) 1307.

[27] Using $\Delta H_f^0[CH_2=COH^{\oplus}] = 898$ kJ/mol: R. Nobes, L. Radom, *Org. Mass Spectrom. 21* (1986) 407.

[28] H. T. Liang, P. D. Bartlett, *J. Am. Chem. Soc. 80* (1958) 3585.