DESTABILIZED CARBENIUM IONS:
α-ACETYL-α,α-DIMETHYLMETHYL CATIONS

ANNE-MARIE DOMMRÖSE and HANS-FR. GRÜTZMACHER *

Fakultät für Chemie, Universität Bielefeld, D-4800 Bielefeld (F.R.G.)

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ABSTRACT

α-Acetyl-α, α-dimethyl cations, **a**, are tertiary carbenium ions destabilized by the electron-withdrawing effect of the acetyl group. Within the family of $C_5H_9O^+$ ions, the ions **a** are less stable than the trimethylacetyl cations, **b**, the protonated 3-methyl-3-buten-2-one ions, **c**, and the protonated 3-pentene-2-one ions, **d**. In spite of this destabilization, the ions **a** can be generated by the loss of a halogen atom from the molecular ions of 3-halo-3-methyl-butan-2-ones **2–4**. The appearance energies (AE) of $C_5H_9O^+$ ions from **2–4** are linearly dependent on the homolytic dissociation energy, $D(C-X)$, and $\Delta H_f(\mathbf{a}) = 596$ kJ mol^{-1} is derived from the AE measurements. The CA spectra of ions **a** and **c** formed by protonation of 3-methyl-3-butene-2-one using CI, are identical and the interconversion of **a** and **c** before fragmentation is corroborated by D-labeling. Ions **a** and ions **c** decompose unimolecularly by loss of CO, giving rise to a broad and dish-topped peak in the MIKE spectrum, in contrast to the fragmentation of other $C_5H_9O^+$ ions. It is suggested that the rearrangement and the elimination of CO from **a** occurs via a 1,2-methyl shift and a corner protonated cyclopropanone as the critical configuration. This reaction path is corroborated by an MNDO calculation of the potential energy hypersurface of $C_5H_9O^+$ ion **a**.

INTRODUCTION

Carbocations are very important intermediates in organic reactions and they have been studied in great detail [1]. Thus, it is well known that the stability and reactivity of carbenium ions depend very much on the nature of the substituents at the centre of the positive charge. Carbenium ions stabilized by electron-donating substituents have been investigated extensively because these ions are easily formed as reactive intermediates and are observed both in solution and in the gas phase. However, there is a second

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* To whom correspondence should be addressed.

class of carbenium ions with an electron-withdrawing substituent attached to the positive centre which increases the electron demand. Thus, the stability of these ions should be decreased: they are "destabilized" carbenium ions. Contrary to earlier expectations, it has been shown that destabilized carbenium ions carrying CF_3, NO_2, RCO, CN, and RSO_2 substituents are also important intermediates in organic reactions and exhibit special reactivities [2]. α-Acyl carbenium ions of the structure $R'CO-\overset{+}{C}R_2$ are of special interest, and, recently, their reactivity in solvolytic reactions has been covered in two reviews [3]. In spite of the electron-withdrawing properties of the acyl group [4], these α-acylcarbenium ions show a quite normal solvolytic reactivity. However, under certain conditions, the substitution is accompanied by rearrangement reactions [5,6]. In view of the interesting properties of destabilized carbenium ions, we have studied their reactions in the gas phase by mass spectrometric techniques to get a better understanding of the reactivity of these species. In the present paper, we report our results on the formation and reactions of α-acetyl-α,α-dimethylmethyl cations $CH_3CO-\overset{+}{C}(CH_3)_2$.

α-Acyl carbenium ions in the gas phase have been reported earlier in the literature [7–10]. The most simple ion of this class is the α-formylmethyl cation, $H-CO-\overset{+}{C}H_2$, and its heat of formation has been theoretically calculated to be 971 kJ mol^{-1} [10]. This leads to a hydride ion affinity (HA) of 1291 kJ mol^{-1}. Compared with the HA of the methyl cation of 1305 kJ mol^{-1} [11], the α-formylmethyl cation appears not to be much "destabilized" in a thermodynamical sense. Obviously, the electron-withdrawing effect of the formyl group is compensated by an increased polarizability of this group compared with a H atom. This shows that the term "destabilization" is more useful with respect to the high reactivity of these ions. Indeed, it is shown both theoretically [10] and by experiment [12], that the α-formylmethyl cation rearranges without an activation barrier into its most stable isomer, the acetyl cation.

The next highest homologue in the series of the α-acyl carbenium ions is the α-acetylmethyl cation. We have tried to generate this ion in the gas phase from suitable precursors by electron impact (EI) and chemical ionization (CI). However, a close inspection of the fragmentation reactions leading to these $C_3H_5O^+$ ions reveals rearrangement reactions during their formation [13]. Thus, the structure of these ions is not known, although their collisional activation (CA) spectra resemble that of the methyloxiranylium ion and are different from the CA spectra obtained by charge reversal of the acetone enolate ion [14]. Obviously, the *primary* α-acylmethyl cations exhibit an extraordinary reactivity [7b]. The α-acetyl-α,α-dimethyl cation **a**, is a *tertiary* carbenium ion, which carries two electron-donating methyl groups

at the positive centre beside the electron-withdrawing acetyl substituent. This "push–pull" substitution may give some stability to this α-acyl carbenium ion so that it may exist as a discrete species in spite of its high inherent reactivity. $C_5H_9O^+$ ions have been studied before [7a,15], but mainly with respect to the structure of the most stable isomer besides the valeroyl cation. The present study focusses on the formation and reactions of the destabilized α-acyl carbenium ion strucutre of this series.

EXPERIMENTAL

Mass spectrometry

The EI mass spectra were obtained with a mass spectrometer/data system MAT 311A/SS 200 [41] under the following conditions: electron energy, 70 eV; electron emission, 2 mA; acceleration voltage, 3 kV; ion source temperature, ca. 180°C; sample introduction by the heated inlet system, 180°C. The CI mass spectra were measured with a GC/MS system Finnigan MAT 1020 B [41] using methane and isobutane, respectively, as a reactant gas at an ion source pressure of ca. 0.3 Torr. Metastable ions have been investigated with a mass spectrometer VG ZAB 2F [42] equipped with a combined EI/CI ion source. The samples were introduced via a heated inlet system at 150°C. The following conditions were used for ion generation by EI: electron energy, 70 eV; electron trap current, 50 μA; acceleration voltage, 6 kV; ion source temperature, ca. 180°C. Methane and tetradeuteromethane were used as reactant gases for ion generation by CI. The electron energy and electron emission current for the generation of the CI plasma were 50 eV and 0.5 mA, respectively. The reactant gas was introduced into the ion source at such a flow rate that the reading at the ion source pressure gauge was around 0.5×10^{-4} Torr. Under these conditions, the ion source temperature stabilized itself at approximately 200°C. The acceleration voltage was 6 kV.

For the detection of the unimolecular fragmentations of the metastable ions, the relevant ion was magnetically focussed into the second field-free region (2nd FFR) of the ZAB 2F mass spectrometer with the ion source slit and the final slit at the detector closed to get a triangular peak of approximately 30% of the intensity with open slits. Under these conditions, the mass resolution is somewhat above 1000. The metastably formed product ions were detected by scanning the voltage at the electrostatic analyzer and recording the mass analyzed ion kinetic energy (MIKE) spectra. The values given for the intensities of the product ions are the mean values of at least three measurements and the deviations for the more intense peaks (> 10% of the base peak) are < 5%.

The kinetic energy release (KER) associated with the fragmentation of metastable ions has been measured in the same way as the MIKE spectra by scanning slowly across the corresponding peak. The KER for the reaction $m_1^+ \rightarrow m_2^+ + m_3$ has been calculated from the width, **d**, of the peak at 50% of its intensity by the formula

$$T = \frac{m_1^2 \left(U_B^0\right)}{16 m_2 m_3 \left(U_A^0\right)^2} \left[\sqrt{d^2 - \left(d_0 \frac{m_2}{m_1}\right)^2} \right]^2$$

where d is the width of the signal in the MIKE spectrum, in V; d_0 is the width of the main beam in the MIKE spectrum, in V; U_B^0 is the acceleration voltage for focussing the main beam, in V; and U_A^0 is the voltage at the electrostatic analyzer for focussing the main beam, in V. The values given for the KER (T_{50}) are the mean values of at least three measurements and the deviations for the broad and dish-topped peaks are $< 3\%$. The peak form of apparently Gaussian-shaped peaks has been checked by the method given by Holmes and Terlouw [16].

The collisionally induced dissociations (CA spectra) were investigated by the same technique used for the MIKE spectra but by introducing He as the collision gas into the collision cell, located in the 2nd FFR, at a flow rate reducing the main beam intensity to ca. 30%.

The ionization energies (IE) and appearance energies (AE) were obtained with a modified mass spectrometer VG MM 12 B [42] equipped with a magnetic peak jumping unit operated under computer control [17]. Fast sequential measurements of the ion yield curves of a reference (methyl iodide, IE = 9.53 eV [18]) and of 8 other ions are possible within 5 min or less, thus minimizing the problems due to fluctuations of potentials in the ion source. The IE and AE have been evaluated by the "semi-log" method [19] using a computer program. The reproducibility of the IE and AE values was ± 0.1 eV.

Compounds

The structure of the compounds used in this study has been verified by ^{1}H-NMR spectroscopy and their purity controlled by gas chromatography.

3-Methyl-butan-2-one and 3,3-dimethyl-butan-2-one (**1**) are commercially available. Repeated treatment of **1** with $D_2O/NaOD$ gives 3,3-dimethyl-butan-2-one-1,1,1-d_3 (**1-d_3**).

3-Chloro-3-methyl-butan-2-one (**2**) was prepared by the chlorination of 3-methyl-butan-2-one with sulphuryl chloride [20]; yield 71%, b.p. 120°/760 Torr.

3-Bromo-3-methyl-butan-2-one (**3**) was obtained from 3-methyl-butan-2-

one by reaction with Br_2 in ether [21]; yield 85%, b.p. $140°/760$ Torr.

3-Iodo-3-methyl-butan-2-one (**4**) was synthesized from the enol acetate of 3-methyl-butan-2-one [22]; yield 80%. The product was used without purification by distillation because of the thermal lability of **4** [23].

3-Hydroxy-3-methyl-butan-2-one (**5**) was obtained by the hydrolysis of **3** according to a method given by Aston and Greenberg [24]; yield 68%, b.p. $50°/18$ Torr.

3-Methoxy-3-methyl-butan-2-one (**6**) was prepared by the methylation of **5** with CH_3I/NaH in THF [25]; yield 73%, b.p. $120°/760$ Torr.

3-Methyl-3-buten-2-one (**7**) was synthesized via an aldol reaction of butan-2-one and formaldehyde and the subsequent dehydration of the product by treatment with H_3PO_4 and Cu powder [26]; yield 47%, b.p. $96°/760$ Torr.

2,3-Dimethyl-2,3-epoxybutane (**8**) was synthesized according to a method given by Delacre [27]; yield 41%; b.p. $90°/760$ Torr.

Trimethylacetic acid ethylester (**9**) was commercially available and was used without further purification.

RESULTS AND DISCUSSION

Stability of $C_5H_9O^+$ ions

The structures of the isomeric $C_5H_9O^+$ ions relevant to the present discussion of the α-acetyl-α,α-dimethylmethyl cation, **a**, are shown in Scheme 1. The heats of formation of these ions obtained from MNDO calculations and derived experimentally from AE and PA measurements are given in Table 1. The comparison of theoretical and experimental values of ΔH_f, where possible, shows that the MNDO values are always too large by 80–120 kJ mol^{-1}. It is known that the calculation of ΔH_f by MNDO may include systematic errors [28] and, in the present case, one has to be careful not to use a mixed scale of theoretical and experimental ΔH_f values for the
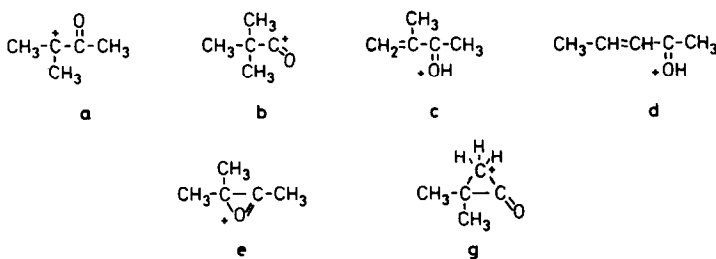
Scheme 1.

TABLE 1

Heats of formation, ΔH_f, of the $C_5H_9O^+$ ions a–e and g

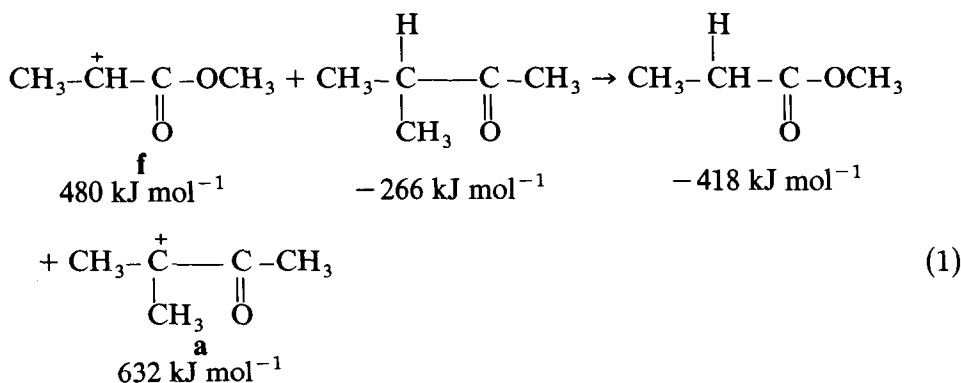| Ion	ΔH_f (kJ mol^{-1})		Ion	ΔH_f (kJ mol^{-1})	
	Exptl.	MNDO		Exptl.	MNDO
a	596	706	d	490 [15c]	
b	502 [a]	625	e		755
c	502 [b]	585	g		854

[a] Ref. 18.
[b] Ref. 15c.

discussion of the relative stability of $C_5H_9O^+$ ions. However, even restriction to one set of ΔH_f values gives only a semi-quantitative picture of the $C_5H_9O^+$ system because of the uncertainties associated with the methods used. Nevertheless, this semi-quantitative scale of the relative stabilities of the $C_5H_9O^+$ ions gives some useful information for an understanding of the reactions of these ions [28].

The most stable species of the series (Scheme 1) is the protonated 3-penten-2-one, **d**, which is slightly more stable than the protonated 3-methyl-butan-2-one, **c**. The experimental values of ΔH_f have been derived from PA measurements of the corresponding ketones [15c], which usually give reliable values. The experimental ΔH_f of the trimethylacetyl cation **b** has been calculated from the AE of adequate precursors [18a] and corresponds to that of **c**, while MNDO predicts a lesser stability for **b**. The stabilization of the positive charge in **b** occurs mainly by the acylium ion structure and only to a lesser extent by the methyl substituents in the β position of the charge. As expected, the ΔH_f of **a** is higher than that of **b–d** in spite of the stabilization by the two methyl groups, reflecting the electron-withdrawing effect and the destabilization by the α-acetyl group. The value of $\Delta H_f(\mathbf{a})$ was derived from the AE of the $C_5H_9O^+$ ions from 3-iodo-3-methyl-butan-2-one, **4**, (see below) using $\Delta H_f(\mathbf{4}) = 200$ kJ mol^{-1} [18b] and $\Delta H_f(\mathbf{I}) = 106$ kJ mol^{-1} [18b]. The AEs of these ions from 3-chloro-3-methyl-butan-2-one, **2**, and 3-bromo-3-methyl-butan-2-one, **3**, as well as that of the $[M-CH_3]^+$ ions of 3,3-dimethylbutan-2-one-1,1,1-d_3, **1**-d_3, lead to higher values of $\Delta H_f(\mathbf{a})$ (637 and 657 kJ mol^{-1}, respectively), but the formation of the $C_5H_9O^+$ ions from **1–3** is a minor process and the AEs are influenced by competitive shifts.

The α-carbomethoxy-α-methylmethyl cation, **f** [see Eq. (1)], which is formed from α-iodopropionic acid methyl ester by electron impact [29], is the only α-acyl carbenium ion known and a ΔH_f of 480 kJ mol^{-1} is reported in the literature [29]. This can be used to calculate ΔH_f (**a**) by the
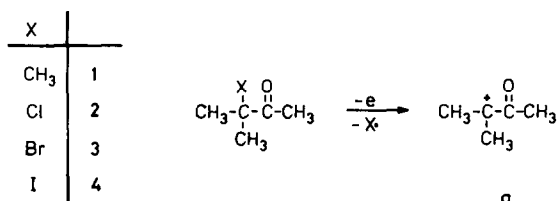
isodesmic reaction

$$CH_3-\overset{+}{CH}-\underset{O}{\overset{\|}{C}}-OCH_3 \ + \ CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}\!\!-\!\!-\!\!-\underset{O}{\overset{\|}{C}}-CH_3 \ \rightarrow \ CH_3-\underset{}{\overset{\overset{H}{|}}{CH}}-\underset{O}{\overset{\|}{C}}-OCH_3$$

f
480 kJ mol^{-1} -266 kJ mol^{-1} -418 kJ mol^{-1}

$$+ \ CH_3-\underset{\underset{CH_3}{|}}{\overset{+}{C}}\!\!-\!\!-\!\!-\underset{O}{\overset{\|}{C}}-CH_3 \tag{1}$$

a
632 kJ mol^{-1}

The value of $\Delta H_f(\mathbf{a})$ obtained from Eq. (1) is in reasonable agreement with the value derived from the AE. Finally, the MNDO calculations also indicate, that $\Delta H_f(\mathbf{a})$ should be 80–120 kJ mol^{-1} larger than $\Delta H_f(\mathbf{b})$ and $\Delta H_f(\mathbf{c})$. Using $\Delta H_f(\mathbf{a}) = 596$ kJ mol^{-1} and $\Delta H_f[(CH_3)_2CHCOCH_3] = -262$ kJ mol^{-1} [18b], one can calculate the HA of **a** to be 997 kJ mol^{-1}, 28 kJ mol^{-1} larger than HA$[(CH_3)_3C^+] = 969$ kJ mol^{-1} [11]. This clearly shows the destabilization of **a** by the electron-withdrawing acetyl substituent.

The ΔH_f of the trimethyloxiranyl cation, **e**, is obtained only by an MNDO calculation. The loss of a methyl group from the molecular ions of 2,3-dimethyl-2,3-epoxybutane, **8**, gives rise to a mixture of ions **a** and **b**, as will be shown below, and not to the oxiranylium ion **e**. Hence, it is not possible to calculate $\Delta H_f(\mathbf{e})$ from the corresponding AE. The easy rearrangement of **e** into **a** and **b** corroborates the prediction of MNDO, however, that **e** is less stable than **a**. This is quite different from the primary α-acetylmethyl cation, which is (by MNDO) less stable than the corresponding oxiranyl ion and obviously rearranges very quickly into this latter ion [13]. This reversed order of stability of the α-acetyl carbenium ions and the oxiranylium ions in the case of the primary and tertiary ions clearly reflects the effect of the "push–pull" substitution of ion **a**.
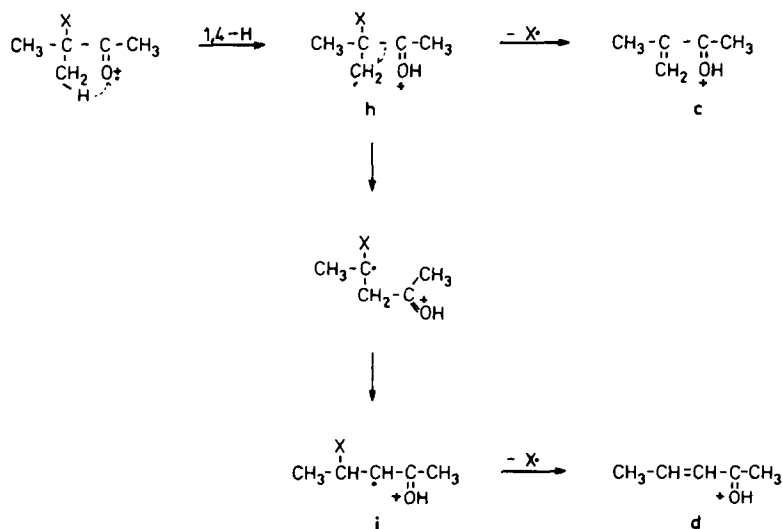
*Formation of the α-acetyl-α,α-dimethylmethyl cation **a***

The α-acetyl-α,α-dimethylmethyl cation **a** should arise from 3-substituted 3-methyl-butan-2-one ions $\mathbf{1^{+\cdot}}$–$\mathbf{4^{+\cdot}}$ by loss of the substituent via a direct bond cleavage as shown in Scheme 2. However, the loss of the substituent adjacent to a carbonyl group from the molecular ions may also occur by the rather complicated rearrangement shown in Scheme 3 which leads to the stable ion **d**. This mechanism has been proven for the loss of $X = CH_3$ from the molecular ions of carboxylic acids and their esters [30] and has been

X	
CH$_3$	1
Cl	2
Br	3
I	4

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{X}{|}}{C}}-\overset{\overset{O}{||}}{C}-CH_3 \quad \xrightarrow[-X\cdot]{-e} \quad CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{+}{\cdot}}{C}}-\overset{\overset{O}{||}}{C}-CH_3$$

a

Scheme 2.

suggested for the molecular ions of ketones [15]. The key step of this mechanism is the 1,4-hydrogen migration within the molecular ions to give the distonic ions **h**. At least in the case of the carboxylic acids and esters, this is the reaction step with the highest activation barrier. Ions **h** rearrange further by a fast 1,2-shift of the group C(OH)CH$_3$ [or C(OH)OR in the case of an acid or ester] and a 1,2-H shift to the enolic ions **i** which eventually lose X . Burgers et al. [29] have shown that it depends on the nature of the substituent X of α-substituted propionic acid methyl esters whether the loss of X occurs by the mechanism shown in Scheme 2 or that of Scheme 3. The nucleophilic CH$_3$ radical is lost only via the route of Scheme 3, while the more electrophilic halogen atoms are lost either by both mechanisms (X = Cl, Br) or for X = I by a direct bond cleavage (Scheme 2). Probably, this effect of X is not due to charge localization [29] but to a variation of the dissociation energy of the C–X bond. The activation energy of the 1,4-H

$$CH_3-\overset{\overset{X}{|}}{\underset{\underset{H}{\underset{|}{CH_2}}}{C}}-\overset{\overset{\cdot}{}}{C}-CH_3 \quad \xrightarrow{1,4-H} \quad CH_3-\overset{\overset{X}{|}}{\underset{\underset{+}{CH_2}}{C}}-\overset{}{\underset{OH}{C}}-CH_3 \quad \xrightarrow{-X\cdot} \quad CH_3-\overset{\overset{X}{|}}{C}-\overset{}{\underset{OH}{C}}-CH_3$$

$$\qquad\qquad\qquad\qquad\qquad\qquad \textbf{h} \qquad\qquad\qquad\qquad\qquad\qquad \textbf{c}$$

$$\downarrow$$

$$CH_3-\overset{\overset{X}{|}}{\underset{\underset{CH_2-C}{}}{C}\cdot}\overset{CH_3}{\underset{OH}{\diagdown}}$$

$$\downarrow$$

$$CH_3-\overset{\overset{X}{|}}{CH}-\overset{}{\underset{+OH}{CH}}-C-CH_3 \quad \xrightarrow{-X\cdot} \quad CH_3-CH=CH-\overset{}{\underset{+OH}{C}}-CH_3$$

$$\qquad\qquad\qquad \textbf{i} \qquad\qquad\qquad\qquad\qquad\qquad \textbf{d}$$

Scheme 3.

TABLE 2

Ionization energies (IE) for **1-4**, appearance energies (AE) of $C_5H_9O^+$ ions, and dissociation energy [D(C–X)]

	IE(M) (eV)	AE($C_5H_9O^+$) (eV)	D(C–X) (kJ mol^{-1})
1	9.4	11.35	342
2	9.7	11.2	336
3	9.55	10.4	277
4	9.2	9.35	211

shift (Scheme 3) within the molecular ion does not depend heavily on X and the direct bond cleavage (Scheme 2) competes with or is favoured over the rearrangement if the C–X dissociation energy is lower. It can be shown [31] that the branching between the mechanisms of Schemes 2 and 3 depends not only on X but also on the PA of the carbonyl group because an increasing PA of the carbonyl group lowers the activation energy of the 1,4-hydrogen shift.

The PA of a ketone is smaller than that of an ester [32]; hence, the activation energy of the 1,4-H shift according to Scheme 3 should be larger for a ketone than for an ester molecular ion. Furthermore, the direct cleavage (Scheme 2) within the molecular ions of **1–4** gives rise to tertiary carbenium ions, whereas Burgers et al. [29] have generated secondary carbenium ions. Both effects should favour the direct loss of the substituent X in the case of the ketones studied here. This can be tested by measuring the AE of the $C_5H_9O^+$ ions from **1–4**, which are expected to depend linearly on the homolytic C–X bond dissociation energy in the case of a direct bond cleavage (Scheme 2), but should be more or less constant in the case of an energy-determining 1,4-hydrogen shift (Scheme 3). The results are shown in Table 2 and in Fig. 1. It is clearly seen that the AEs depend linearly on the bond dissociation energy D(C–X) of X bound to a tertiary butyl group [33,34].

The AE of $C_5H_9O^+$ ions from the bromoketone **3** has been determined before by Bouchoux and Dagaut [15a] and our value is in good agreement with their AE of 10.35 eV. However, the conclusion drawn by these authors from this one value concerning the mechanism of the $C_5H_9O^+$ ion formation is wrong because a rate-determining 1,4-hydrogen shift (Scheme 3) can not explain the observed variation of the AE values with the leaving group X. This clearly demonstrates the pitfalls one can encounter by using only one AE measurement and a mixed energy scale of experimental and MNDO values [15a].
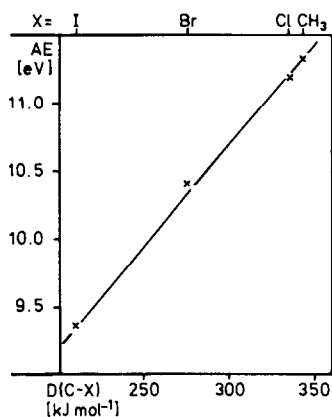
Fig. 1. Dependence of $AE(C_5H_9O^+)$ from $(CH_3)_2CX-COCH_3$ 1–4 (X = CH_3, Cl, Br, I) on the homolytic bond dissociation energy $D(C-X)$.

The ions **a** should also arise from the protonated molecules MH^+ of appropriately 3-substituted 3-methyl-butan-2-ones by loss of HX in a CI experiment (Scheme 4). In the CI(methane) mass spectra of **2–4**, the $C_5H_9O^+$ ions are very intense and give rise to the base peak in the spectra of 3-hydroxy-3-methyl-butan-2-one **5** and 3-methoxyl-3-methyl-butan-2one **6**. The formation of **a** by HX elimination from MH^+ avoids a radical cation precursor which rearranges by hydrogen migrations. However, formation of **a** requires proton addition to X during CI [path (a) in Scheme 4], and, at least for **2–4** (X = Cl, Br, I), the carbonyl group is the most basic group within the molecules. Protonation at the carbonyl group may initiate a "quasi-thermal" 1,2-elimination of HX if sufficient excess energy is available in MH^+. This elimination gives rise to $C_5H_9O^+$ ions of structure **c** [path (b) in Scheme 4]. Both elimination mechanisms can be differentiated by using CD_4 as the reactant gas during CI. In this case, a D^+ is transferred to the
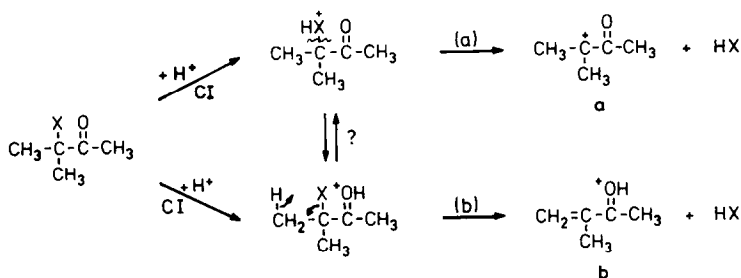
Scheme 4.
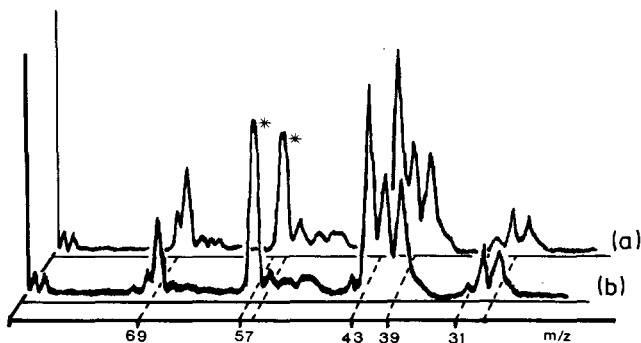
Fig. 2. CA spectra of $C_5H_9O^+$ ions **a** derived from 3-bromo-3-methyl-butan-2-one, **3**, (a) by EI and (b) by CI. * indicates loss of CO, occurring also unimolecularly.

molecules and only DX is eliminated via path (a) (Scheme 4), whereas elimination via path (b) results in the loss of HX from MD^+. Indeed, the MD^+ ions of **3** eliminate only DX in the ion source and as metastable ions in the 2nd FFR of the ZAB 2F mass spectrometer, thus proving a reaction only by path (a).

In contrast to the haloketones **2–4**, the hydroxyketone **5** and the methoxyketone **6** eliminate HDO and H_2O, and CH_3OD and CH_3OH, respectively, from the MD^+ ions so that elimination takes place by path (a) *and* by path (b) (Scheme 4). In the case of **5**, the ratio $HDO/H_2O = 5:1$ is observed for the elimination processes in the ion source and $1:1$ for the decomposition in the 2nd FFR. Similarly, the ratio $CH_3OD/CH_3OH = 4:1$ and $1:1$ is observed for the reactions of the MD^+ ions of **6** in the ion source and in the 2nd FFR, respectively. Hence, the more energetically excited MD^+ ions prefer a fast reaction by a direct bond cleavage according to path (a), whereas path (b) can compete more effectively in the slow reactions of metastable ions with low internal energy. This is in agreement with the proposed elimination mechanisms since path (b) leads to the more stable product ion **c** but via a more "tight" 4-membered cyclic transition state.

The CA spectra of the $C_5H_9O^+$ ions generated from **2–6** by EI and by CI, respectively, are identical and two examples are shown in Fig. 2. The most intense fragmentations are the loss of CO, which also occurs unimolecularly (see below), and the formation of CH_3CO^+ ions, m/z 43. The identity of the CA spectra is of special importance for the $C_5H_9O^+$ ions arising from **3** by EI-induced loss of Br⁻ and by loss of HBr during CI. The elimination of HBr from MH^+ of **3** occurs without any sign of a rearrangement and thus gives ions **a**. Hence, it can be concluded that the $C_5H_9O^+$ ions in the EI mass spectrum of **3** and the other $C_5H_9O^+$ ions derived from **2–6** are also of this structure. The exceptions are the $C_5H_6D_3O^+$ ions generated from **1-**d_3 by
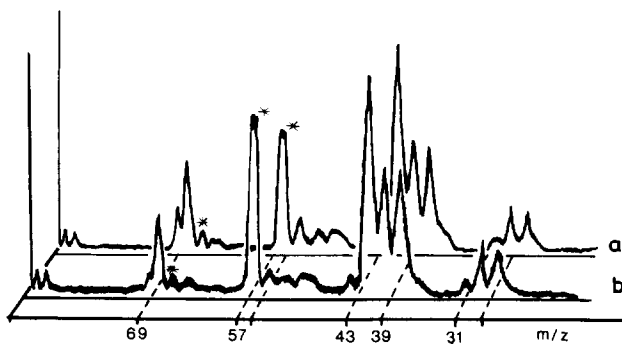
Fig. 3. CA spectra of $C_5H_9O^+$ ions **a** (from 3-iodo-3-methylbutan-2-one **7** by CI). * = observed also as an unimolecular reaction.

EI. The MIKE spectrum of these ions differs by a large signal due to loss of H_2O (and HDO), which is the characteristic reaction of ions *d* [15]. Obviously, ions *d* are formed as well as ions **a** by loss of a CH_3 radical from $1\text{-}d_3$, in agreement with earlier observations.

Reactions of the α-acetyl-α,α-dimethylmethyl cation

Reactions of α-acetyl-α,α-dimethylmethyl cations of low internal energy in the gas phase are of interest with respect to the reactivity of α-acyl carbenium ions in solution [2,3]. In the previous section, it was shown that the MH^+ of compounds **5** and **6** form $C_5H_9O^+$ ions by paths (a) and (b). Hence, these ions should be a mixture of the structures **a** and **c**. In spite of this, the CA spectra of these ions can be superimposed on those of the $C_5H_9O^+$ ions generated from the other compounds. An explanation for this result would be the mutual interconversion of ions **a** and **c** before fragmentation. This isomerization can be studied by generation of ions **c** independently by protonation of 3-methyl-3-buten-2-one, **7**, in a CI experiment. The protonation of **7** is known to give $C_5H_9O^+$ ions of structure **c** [15b,c]. The CA spectrum of the MH^+ of **7** obtained by CI(methane) is compared with that of the $C_5H_9O^+$ ions derived from the iodoketone **4** in Fig. 3 (see also Fig. 2 for further CA spectra). The only difference observed is the intensity of the peak due to loss of CO, which is by far the most intense peak in the MIKE spectra of these ions. Otherwise, the identity of the CA spectra is strong evidence that the $C_5H_9O^+$ ions of both origins are of the same structure or the same mixture of structures. This either means that ions **c** are also generated from the other compounds **2–6**, contrary to the discussion in the previous section, or that the ions **a** and **c** freely interconvert by 1,4-hydrogen migrations. The interconversion between ions **a** and **c** is
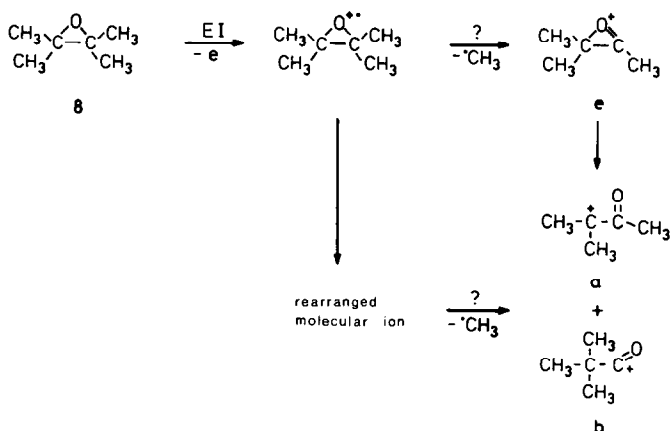
Scheme 5.

corroborated by the CA spectrum of the MD^+ ions of **7** obtained by CI(tetradeuteromethane). The mass shifts observed in this spectrum indicate the incorporation of the D atom originally at the deuteronated carbonyl group into the hydrocarbon fragment ions, but no incorporation into the ion m/z 43, which are very likely acetyl ions. This can be explained by a migration of the D^+ from the carbonyl group to the β-C atom of the α,β-unsaturated ketone moiety of ion **c**.

The present result of an interconversion of ions **a** and **c** indeed shows that the 1,4-hydrogen shift discussed in the literature [15] occurs but, instead of an irreversible H transfer in the molecular ions, it is a reversible H migration in the fragment ions. The protonated α,β-unsaturated ketone **c** is more stable than the α-acyl carbenium ion by ca. 100 kJ mol^{-1} and, hence, ion **c** is favoured in the equilibrium mixture, especially at low internal energies. Nevertheless, the destabilized α-acyl carbenium ion **a** must also be a stable entity in a potential energy well as shown by the results in the previous section. However, the activation barrier separating ions **a** and **c** is not known and may, in fact, be rather small. Another ion structure which could be in equilibrium with ion **a** is the trimethyloxiranylium ion **e**. We have tried to generate ion **e** via loss of a methyl radical from the molecular ions of 2,3-dimethyl-2,3-epoxybutane **8** (Scheme 5) and the CA spectrum of the $C_5H_9O^+$ ions thus formed is compared with those of ions **a** and of the trimethylacetyl ions **b** in Fig. 4. The latter ion is also a stable $C_5H_9O^+$ isomer and has been formed by loss of the CD_3 group of the molecular ions of 1-d_3 and loss of $C_2H_5O \cdot$ from the molecular ions of trimethylacetic acid ethyl ester **9**, respectively.

The CA spectrum of **b** is distinguished from that of ions **a** (and **c**) by the absence of the peak of the acetyl ions at m/z 43, which is in good agreement

Fig. 4. CA spectra of $C_5H_9O^+$ ions **a** (from 3-bromo-3-methylbutan-2-one, **3**), ions **b** (from 3,3-dimethyl-butan-2-one-1,1,1-d_3, **1**-d_3), and ions **e** (from 2,3-dimethyl-2,3-epoxybutane, **8**).
* = observed also as an unimolecular reaction.

with the proposed structures of these ions. Furthermore, the peak shape for the signal due to the loss of CO which also occurs unimolecularly is a narrow Gaussian for **b** but broad and dish-topped for **c**. The CA spectrum of the $C_5H_9O^+$ ions derived from **9** and expected to represent ions **e** differs from that of ions **a** by a reduced intensity of the fragment ions m/z 43 by an additional signal due to loss of H_2O and by the peak shape of the signal for CO loss, which is clearly composite. The reduced intensity of m/z 43 and the presence of a narrow component in the peak for loss of CO can be accounted for by the presence of ions **b** (ca. 20%) and the peak due to loss of H_2O can be attributed to an admixture of a small amount of ions **d**. Thus the $C_5H_9O^+$ ions from **8** are a mixture of ions with different structures in which ions **a** probably dominate. A ring opening of ions **e** to ions **a** is in agreement with the relative stabilities of these ions calculated by MNDO

(see first section). However, there must also be a rearrangement by a 1,2-methyl shift to form ions **b**. Ring opening and rearrangements in the EI mass spectra of oxiranes have been discussed before [35,36], but it is not definitely known whether the reactions occur in the molecular ions or in the fragment ions.

All the $C_5H_9O^+$ ions studied fragment unimolecularly by the elimination of CO and, with the exception of ions **d**, this is by far the most intense reaction. However, the kinetic energy release (KER) associated with this reaction is very different. The T_{50} values for ions **a**, **b**, and **c** generated from different precursors and the T_{50} value for the $C_5H_9O^+$ ions derived from the oxiran **8** are given in Table 4 and the different peak shapes of the corresponding signal in the MIKE spectra are shown in Fig. 5. The peak for CO loss from ions **b** is very narrow and the small KER of 6 meV agrees well with that observed for CO loss from other acylium ions without rearrangement [37]. In contrast to this, the elimination of CO from ions **a** and **c** gives rise to a broad and dish-topped peak, indicating a non-statistical KER during this process. Finally, the composite nature of the peak for CO loss from the $C_5H_9O^+$ ions generated from **8** is clearly seen by the small narrow peak sitting at the top of a broad dish-topped peak (Fig. 5). The KER measured for the broad component agrees with that obtained from the peaks for CO loss from **a** and **c**, corroborating the assumption that these ions are present in the mixture of $C_5H_9O^+$ ions **8**.

The KERs measured for the elimination of CO from $C_5H_9O^+$ ions in the EI mass spectra of the α-substituted ketones 1–4 are identical within the limits of error.Therefore, $T_{50} = 315 \pm 10$ meV is characteristic for the reaction of these ions **a**. If the $C_5H_9O^+$ ions are formed by CI, the increase in $T_{50} = 350 \pm 10$ meV can be attributed to the poorer resolution during these experiments. The peak in the MIKE spectra of $C_5H_9O^+$ ions originally

TABLE 3

T_{50} for loss of CO from $C_5H_9O^+$ ions

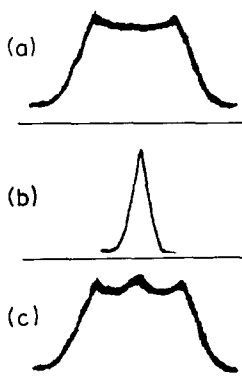| Precursor	Method	Structure	T_{50} (meV)
2	EI(−Cl)	a	325
3	EI(−Br)	a	315
4	EI(−I)	a	315
5	CI(isobutane)	a	350
6	CI(isobutane)	a	350
7	CI(isobutane)	c	295
8	EI(−CH$_3$)		330
9	EI(−OC$_2$H$_5$)	b	6

Fig. 5. Peak shapes for the elimination of CO in the MIKE spectra of (a) ions **a**, (b) of ions **b**, (c) of ions **e**.

formed as ions **c** by protonation of **7** is also broad and dish-topped. The value of $T_{50} = 290 \pm 10$ meV is just below that measured for ions **a**. Obviously, these small variations in T_{50} by otherwise similar peak shapes are due to variations in the experimental conditions and probably in the internal energy of the $C_5H_9O^+$ ions and are not indicative of different critical configurations for the elimination of CO. Thus, the elimination of CO from ions **a** and **c** occurs via the same critical configuration, which is further proof for the mutual isomerization at internal energies below the potential energy of the critical configuration of the CO elimination.

The loss of CO from α-acyl carbenium ions is of interest with respect to the rearrangement reactions of these ions in solution [3,5,6]. In certain cases the rearrangement product of an 1,2-alkyl shift or an 1,2-aryl shift across the carbonyl group is observed in addition to the normal substitution product. A similar 1,2-migration of the group adjacent to the carbonyl group towards the carbenium ion centre has to precede the elimination of a CO molecule from the α-acyl carbenium ion in the gas phase. The migration of a phenyl group and loss of CO has already been observed for metastable α-benzoyl carbenium ions [7]. The elimination of CO accompanied by migration of alkoxy groups in α-carbalkoxy carbenium ions is known from the EI mass spectra of α-bromoesters [31,38] and the CI mass spectra of α-hydroxyesters [39]. In each case, the elimination of CO from tertiary α-acyl carbenium ions is associated with large and non-statistical KERs [7,31]. This indicates a process with a tight transition state having a large reverse activation energy. The rearrangement of the α-acetyl-α,α-dimethylmethyl cation **a** occurs by 1,2-shift of a methyl group as shown in Scheme 6 and the critical configuration for this process is identical or very similar to the structure **g** [7a].
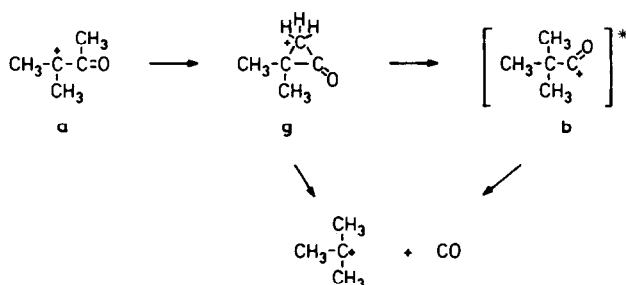
Scheme 6.

Starting from the more stable ion **c**, the 1,4-hydrogen shift to ion **a** precedes the further reaction and it has been suggested, based on an MNDO calculation of the MERP [15], that the transition state of this hydrogen shift is the origin of the KER during CO loss. However, this assumption is at variance with the other experimental results indicating an equilibrium between **a** and **c** at internal energies below the activation energy for CO loss. Furthermore, a large non-statistical KER is also observed for the CO loss from α-acetyl benzyl ions which can not react by a preceding hydrogen rearrangement [40].

The critical configuration **g** for the loss of CO corresponds to a corner-protonated cyclopropanone. Corner-protonated cyclopropanes are known to be intermediates (or transition states) of the rearrangements of carbenium ions in superacidic solutions by 1,2-shifts of methyl groups [1].

A value for $\Delta H_f(\mathbf{g})$ is not available and would be difficult to get, but by MNDO, **g** is 149 kJ mol^{-1} higher in energy than **a**, as expected for a critical configuration, and 229 kJ mol^{-1} above the trimethylacetylation **b**, which would be the rearranged product. Hence, there exists a very large reverse activation energy as indicated by the large KER. Finally, $\Delta H_f(\mathbf{g})$ is 255 kJ mol^{-1} higher than the sum of the heats of formation of the dissociation products { $\Delta H_f(t\text{-}C_4H_9{}^+) = 710$ kJ mol^{-1} by MNDO. $\Delta H_f(CO) = -111$ kJ mol^{-1} [18a]}, so that a large amount of the reverse activation energy can be released as kinetic energy. However, the acyl ion **b** is not a necessary intermediate on the MERP for the CO loss from **a** but **g** may decompose directly by an expulsion of CO. A direct fragmentation of the rigid ion **g** would be a better explanation for the non-statistical KER since the loss of CO from acyl ions via a loose transition state and accompanied by a rearrangement usually gives broad but more or less Gaussian-shaped peaks in the MIKE spectrum [37].

An interesting feature of the structure of **g** as shown in Fig. 6 is the length of the bond between the carbonyl group and the C atom of the $(CH_3)_2C$
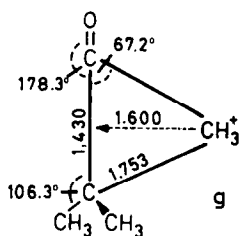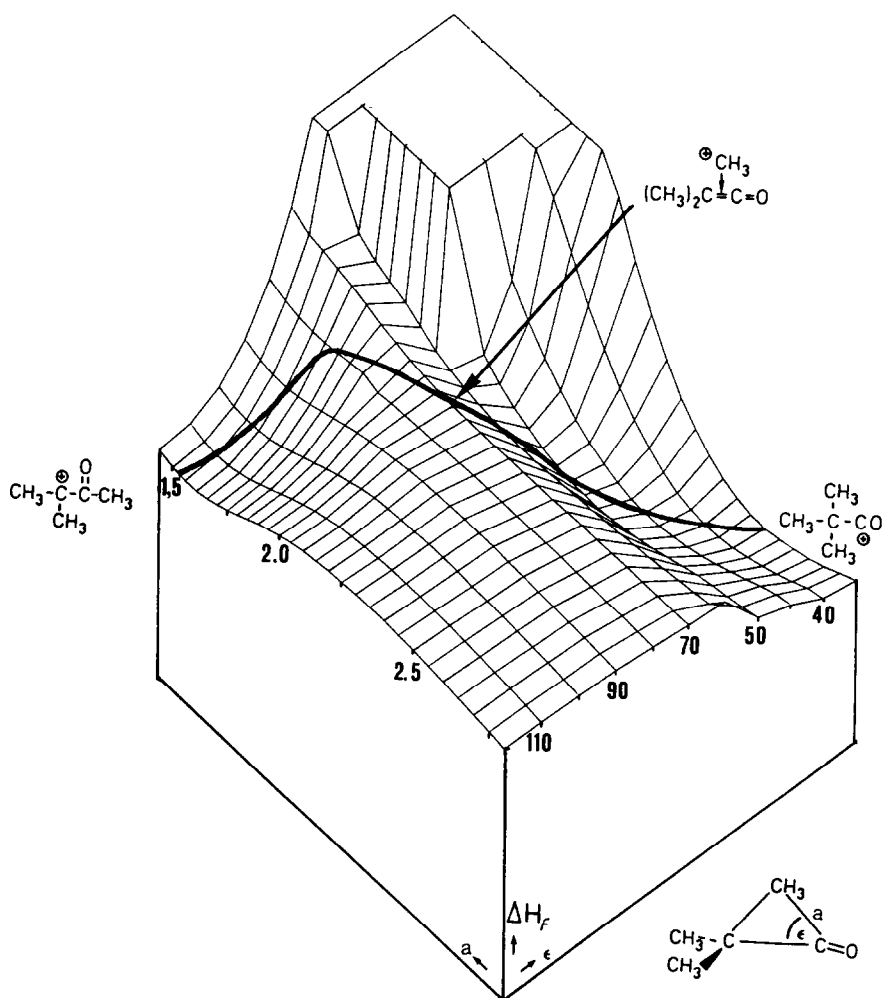
Fig. 6. Geometry (MNDO) of ion **g** (bond lengths in Å)

Fig. 7. MNDO-potential energy hypersurface of the 1,2-methyl shift **a** → **g** → **b**, (a = bond length of CO group to migrating CH$_3$ group; ϵ = bond angle at the CO group).

group, which is rather short for a single bond, and the long bonds to the migrating methyl group. Hence, **g** can be depicted as a π complex of a dimethylketene molecule and a methyl cation. A potential energy hypersurface for the 1,2-methyl migration in **a** has been calculated by MNDO at a fixed bond length of 1.43 Å between the CO group and the $(CH_3)_2C$ group, which is shown in Fig. 7. This surface shows that the energy of **g** is indeed not very sensitive to the distance from the CH_3 group to the rest of the structure and that **g** represents a "ridge" of the energy hypersurface with an especially steep decrease towards the ion **b**.

CONCLUSION

The present study shows that α-acetyl-α,α-dimethylmethyl cations **a** can be formed in a mass spectrometer by electron impact and by chemical ionization from suitable precursors. A prerequisite for the generation of ions **a** is a good leaving group in the precursor at the α-C atom adjacent to the carbonyl group, which can be lost easily with an activation energy below that for a 1,4-hydrogen shift in the molecular ions. This latter reaction is the first step of a rearrangement of the molecular ions leading eventually to the most stable $C_5H_9O^+$ ions of structure **d** [30]. Ion a isomerizes into the more stable protonated 3-methyl-3-buten-2-one **c** by a 1,4-hydrogen shift. The interconversion of ions **a** and **c** is proved by identical CA spectra, which are different from those of the skeletal rearrangement products **b** and **d**. However, the linear dependence of $AE(C_5H_9O^+)$ on the dissociation energy of the leaving group X clearly shows that ions **a**, and not **c**, are generated from the α-halogen ketone precursors.

The mutual isomerization of **a** and **c** occurs at internal energies below those needed for an unimolecular decompositon in the 2nd FFR of a ZAB mass spectrometer, but the height of the energy barrier separating **a** from its more stable isomer **c** is not known. However, there is an energy barrier along the MERP for the unimolecular fragmentation of **a** into the stable *tert.*-butyl cation and CO, which is the energetically most favored reaction of the mixture of metastable ions **a** and **c** and which is associated with a large and non-statistically KER due to a reverse activation energy. While ion **c** is the *most stable structure* within the mixture of interconverting $C_5H_9O^+$ ions, the ion **a** clearly represents the *reactive configuration* from which the *critical configuration* **g** for the elimination of CO can be reached by bending and stretching of bonds but without any further shifts of atoms. The critical configuration **g** corresponds to a corner-protonated dimethylcyclopropanone and its high energy content and its rigid structure is the reason for the large KER during the loss of CO.

Finally, it should be noted that the rearrangement of the α-acetyl-α,α-di-

methylmethyl cations **a** in the gas phase via a 1,2-methyl shift and loss of CO parallels the rearrangements of certain destabilized α-acyl carbenium ions in solution [3,5,6].

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