Kinetic Energy Release during CO Loss by Rearrangement of α-Benzoylcarbenium Ions

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Primary α-benzoylcarbenium ions (a) and tertiary α-benzoyldimethylcarbenium ions (b) are obtained by chemical ionization of ω-hydroxyacetophenone and its dimethyl derivative, respectively. Both α-acylcarbenium ions decompose by a rearrangement reaction and subsequent loss of a CO molecule. The kinetic energy released during this process by metastable ions a and b has been determined under different experimental conditions. The kinetic energy released during the CO elimination from the tertiary α-benzoyl-dimethylcarbenium ions b is independent of the experimental conditions and gives rise to dish-topped peaks with $T_{50} = 440 \pm 20$ meV in the MIKE spectra of b. In contrast to this the kinetic energy releases and the peak-shapes in the MIKE spectra of the primary α-benzoylcarbenium ion a varies with the experimental conditions. The mechanism of this rearrangement reaction is discussed, and it is shown by a MNDO calculation of the heats of formation of the relevant ions that the different characteristics of the kinetic energy release during the fragmentation of primary and tertiary carbenium ions can be attributed to different types of reaction energy profiles.

The Kinetic Energy Release (KER) during the fragmentation of metastable ions gives important information about the reaction hypersurface and the critical configuration of the reacting ion.[1-3] The width of a peak in the Mass analysed Ion Kinetic Energy (MIKE) spectrum and the mean value $\langle T \rangle$ of the translational energy released may increase considerably if a rearrangement of the metastable ions precedes the (last) dissociation step.[4] This effect is explained by a 'rate-determining' rearrangement giving the reacting ion as a chemically activated species which will release its relatively large amount of non-fixed excess energy in a statistical manner. Broad 'flat-topped' or 'dish-topped' signals in the MIKE spectra can be attributed to a potential energy barrier in the last dissociation step of a fragmentation corresponding to a critical energy of the reverse reaction. The fixed potential energy of the reacting ions in the transition state gives rise to a non-statistical distribution of KER. However, a release of large amounts of the reverse critical energy as translational energy T is not always observed. It has been shown[5] that in a series of structurally related ions expected to react by the same fragmentation mechanism large values of $\langle T \rangle$ and a non-statistical KER are observed only for endothermic or thermoneutral fragmentation reactions, while exothermic reactions are associated with statistical KER and rather small values of $\langle T \rangle$ in spite of large reverse critical energies. This 'switch over' from non-statistical KER (T originating mainly from the reverse critical energy) to statistical KER (T originating from the non-fixed excess energy) with the change of the reaction enthalpy is predicted by fundamental theoretical models of chemical reactions[6] and by the correlation of the position of the transition state on the reaction coordinate with the reaction enthalpy.[7]
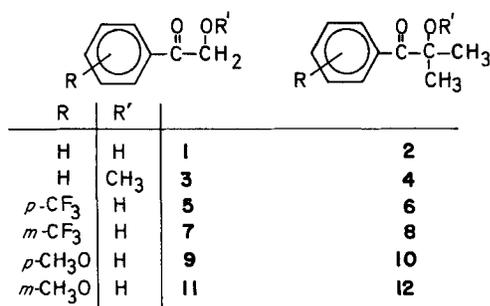
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Recently, we have observed large KERs during the loss of CO from some metastable tertiary α-acylcarbenium ions.[8] In this paper we report on our investigation of this rearrangement reaction of primary and tertiary α-benzoylcarbenium ions corresponding to a quasi-Favorskii rearrangement of these intermediate ions in the condensed phase. Interestingly, a large KER is only observed during the rearrangement of the tertiary ions, while loss of CO from the primary ions occurs with a small KER. Hence, the loss of CO by rearrangement of α-benzoylcarbenium ions is a further example for a dramatic change of the KER during a reaction with a change of the substitution at the reaction centre.

RESULTS

It was observed during a preliminary study of primary and tertiary ω-halogenoacetophenones that these compounds fragment in their EI mass spectra mainly by α-cleavage at the carbonyl group and formation of benzoyl ions and only to a very small extent by loss of the halogen and formation of α-benzoylcarbenium ions. In contrast, the [MH]⁺ ions in the CI mass spectra of ω-hydroxyacetophenones and ω-alkoxy-acetophenones form α-benzoylcarbenium ions with a sufficient intensity for an investigation by MIKE spectroscopy. Hence, the ω-hydroxyacetophenones **1** and **2**, their O-methyl ethers **3** and **4** and some substituted derivatives **5–12** have been chosen as precursors for the α-benzoylcarbenium ions.

The CI (isobutane) mass spectra of **1** and **2** are shown in Fig. 1. Both spectra exhibit a prominent peak for the [MH]⁺ ions indicating that the proton affinity (PA) of these α-ketols is larger than the PA (isobutene), 824 kJ mol⁻¹.[9] No useful CI mass spectra

R	R'		
H	H	1	2
H	CH$_3$	3	4
p-CF$_3$	H	5	6
m-CF$_3$	H	7	8
p-CH$_3$O	H	9	10
m-CH$_3$O	H	11	12

Scheme 1

were obtained with NH$_3$ and CH$_3$NH$_2$ as reagent gases, which puts PA (**1**, **2**) as <858 kJ mol^{-1}.[9]

There is only a small amount of fragmentation in the CI (isobutane) mass spectrum of **1**. Concurrent to the loss of H$_2$O (m/z 119) followed by loss of CO (m/z 91) the formation of benzoyl ions m/z 105 is observed (Scheme 1). As expected by the larger energy transfer during the ionization process, the CI (methane) mass spectrum of **1** shows much more fragmentation and the benzoyl ion gives rise to the base peak. The metastable [MH]$^+$ ions of **1** lose only H$_2$O, but the Collision Induced Dissociation (CID) spectrum of the [MH]$^+$ ion shows signals due to the ions m/z 119, m/z 105, m/z 91, m/z 77 and some m/z 51 as observed in the CI mass spectrum. This shows that all the ions observed originate from the [MH]$^+$ ions and not from electron impact induced dissociation.

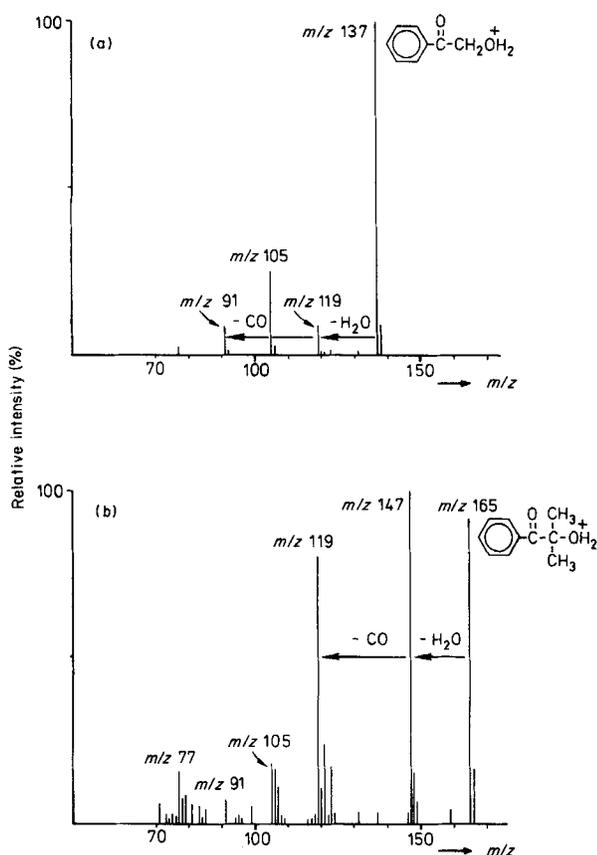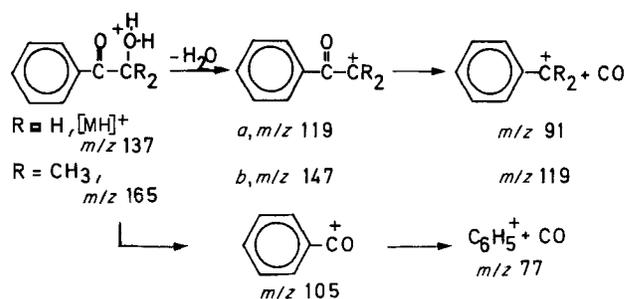The CI (isobutane) mass spectrum of **2** contains large peaks at m/z 147 and m/z 119 of the tertiary

α-benzoylcarbenium ion and its decomposition product, respectively (Scheme 1). The increased fragmentation in the CI mass spectrum of **2** compared to **1** is easily explained by the formation of more stable tertiary carbenium ions.

The loss of H$_2$O is the only reaction observed for metastable [MH]$^+$ ions of **1** and **2**, and in both cases metastable [MH$-$H$_2$O]$^+$ ions show only loss of CO as a further reaction. Hence, this reaction sequence of Scheme 1 is the energetically most favoured decomposition pathway of the protonated α-hydroxyketones. A priori structures different from the α-benzoylcarbenium ions a and b may be assumed for the [MH$-$H$_2$O]$^+$ ions, especially in the case of the tertiary compound **2**. However, in analogy to Scheme 1, loss of CH$_3$OH followed by loss of CO is observed for the [MH]$^+$ ions of the O-methyl ethers **3** and **4**. Furthermore, the derivatives of **2** deuterated at the phenyl group and at both methyl groups, respectively, show only loss of H$_2$O in their CI mass spectra both for unstable [MH]$^+$ ions reacting in the ion source and for metastable [MH]$^+$ ions. Clearly, only the hydroxy group or methoxy group and the proton added during the CI process take part in the first elimination step, and any hydrogen migrations and/or rearrangement reaction occur in the [MH$-$H$_2$O]$^+$ ions.

The values of T measured at half-height of the peak (T$_{50}$) during the loss of H$_2$O and CH$_3$OH, respectively, from the metastable [MH]$^+$ ions **1-4** in the second field free region (2nd FFR) of a VG ZAB 2F mass spectrometer under different conditions are given in Table 1. All signals correspond to a simple Gaussian peak-shape.[10] With the exception of **9** and **10** values of T$_{50}$ = 30 ± 5 meV and simple Gaussian peak-shapes are also obtained for H$_2$O loss from the protonated substituted compounds **5-12**. The somewhat larger T$_{50}$ values of 80 meV for **9** and 40 meV for **12** probably indicate an attachment of the proton to the

Figure 1. CI (isobutane) mass spectra of (a) ω-hydroxyacetophenone (**1**) and (b) α-hydroxyisobutyrophenone (**2**).

Table 1. T$_{50}$ values (meV) during the loss of H$_2$O and CH$_3$OH, respectively, from [MH]$^+$ ions 1-4[a]

Compound	CI (isobutane)	CI (methanol)	CI (methane)
1	30	30	25
2	30	25	25
3	35	30	30
4	30	30	25

[a] All signals correspond to a Gaussian peak-shape with n = 2.0±0.1.[3,10]

Table 2. T_{50} values (meV) during the loss of CO from α-benzoylcarbenium ions a, of 1, 3, 5, 7, 9 and 11, and b, of 2, 4, 6, 8, 10 and 12

Compound	CI (isobutane)	CI (methane)
1	35	230
3	45	250
5	200	—
7	215	—
9	200	—
11	160	—
2	450	450
4	440	410
6	370	—
8	360	—
10	500	—
12	410	—

Figure 3. Metastable peak-shapes for loss of CO from ion a; solid line = CI (isobutane), dashed line = CI (methane).

carbonyl group, which is more basic because of resonance interaction with the *para* methoxy group.

The data for the KER during the loss of CO in the second field free region from the α-benzoylcarbenium ions a and b formed by fragmentation of 1–12 are shown in Table 2. In no case does the peak-shape of the corresponding signals in the MIKE spectra correspond to a Gaussian distribution of the KER. The peak-shapes and the T_{50} values are clearly different for the reactions of primary and tertiary α-benzoyl ions a and b, respectively.

Large values of T_{50} and flat-topped or dish-topped peaks are observed for the CO loss from all tertiary α-benzoylcarbenium ions b. The corresponding peak for the reaction of metastable ions b in the 2nd FFR of the VG ZAB mass spectrometer and generated by the CI (isobutane) mass spectrum of 2 is shown in Fig. 2. An identical peak and an identical KER within the 10% limit of error is obtained for the reaction of ions b derived from the O-methyl ether 4. Furthermore, the peak-shape is not altered if methane is used for the chemical ionization in spite of a much larger excess energy of the original [MH]$^+$ ions. Finally, a dish-topped peak and only slightly larger T_{50} values of 465 ± 15 meV are obtained by observing the rearrangement and CO loss of the tertiary α-benzoylcarbenium ions b from 2 and 4 in the 1st FFR of the VG ZAB instrument by scanning the accelerating voltage. Hence, the KER during the loss of CO from these tertiary α-benzoyldimethylcarbenium ions b is independent of the method of preparation.
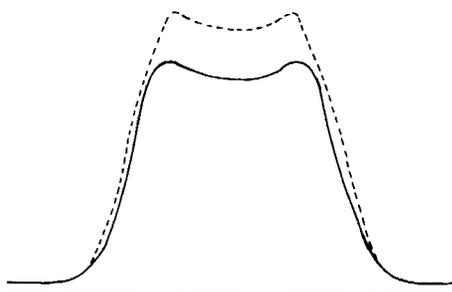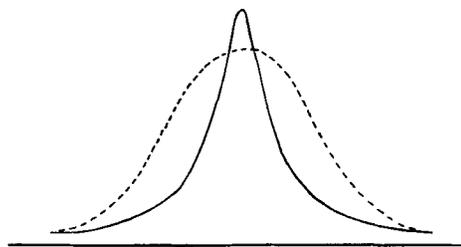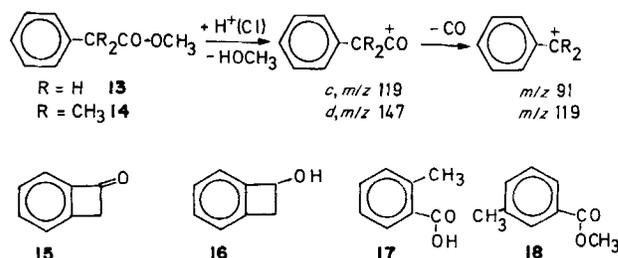
In contrast, the T_{50} values for the loss of CO from the primary α-benzoylcarbenium ion a in the CI mass spectra of 1 and 3 and its substituted derivatives are smaller than for the tertiary ions b and vary with the methods of preparation and observation of the ions. The peak observed for CO loss in the 2nd FFR of the VG ZAB instrument from the primary ion a in the CI (isobutane) mass spectrum of 1 is shown in Fig. 3. A similar signal with this peculiar peak-shape but with a slightly larger T_{50} value may be obtained for the same process in the CI (isobutane) mass spectrum of the O-methyl ether 3. However, it turned out to be experimentally difficult to reproduce this peak-shape. Lowering the pressure of the isobutane in the ion source (increasing the relative concentration of m/z 43 ions in the CI plasma) results in considerable broadening of the peak. Similarly, the use of methanol or methane as reagent gases for preparing the [MH]$^+$ ions gives rise to primary α-benzoylcarbenium ions a which lose CO in the 2nd FFR with a KER corresponding to a more or less triangular peak as indicated in Fig. 3. In the 1st FFR the loss of CO from ion a derived from 1 and 3 always gives rise to a triangular peak and $T_{50} = 300 \pm 20$ meV irrespective of the reagent gas used in preparing the [MH]$^+$ ions. The phenyl-substituted ω-hydroxyacetophenones have been investigated only by CI (isobutane) mass spectrometry and only triangular peaks for the loss of CO from the substituted ions a have been observed.

Phenylacetyl ions (c) and dimethylphenylacetyl ions (d) are possible intermediates during the CO loss of the α-benzoylcarbenium ions, a and b, respectively. These ions are observed with small intensities, together with [MH]$^+$ and [C$_6$H$_5$CR$_2$]$^+$ ions, in the CI mass spectra of methyl phenylacetate (13) and methyl dimethylphenylacetate (14) (see Scheme 2). The loss of CO from these ions also occurs with low intensity in the second FFR and the corresponding T_{50} values are

Figure 2. Metastable peak-shapes for loss of CO from ion b; solid line = CI (isobutane), dashed line = CI (methane).

R = H **13**
R = CH$_3$ **14**

c, m/z 119
d, m/z 147

m/z 91
m/z 119

15   **16**   **17**   **18**

Scheme 2

Table 3. T_{50} values (meV) during the loss of CO in the mass spectra of 13–18

Compound	Ionization method	Precursor ion	T_{50} (meV)	Remarks
13	$CI(CH_4)$	$[MH-H_2O]^+$	100 ⎫	Peak with a
	$CI(C_4H_{10})$	$[MH-H_2O]^+$	100 ⎭	round top
14	$CI(CH_4)$	$[MH-CH_3OH]^+$	~125 ⎫	Very low
	$CI(C_4H_{10})$	$[MH-CH_3OH]^+$	~250 ⎭	intensity
15	$CI(CH_4)$	$[MH]^+$	100 ⎫	Low intensity
	$CI(C_4H_{10})$	$[MH]^+$	120 ⎭	
16	EI(70 eV)	$[M-H]^+$	20	Single Gaussian peak
17	EI(70 eV)	$[M-OH]^+$	30	Single Gaussian peak
18	EI(70 eV)	$[M-OCH_3]^+$	30 ⎫	Single Gaussian peak
	$CI(CH_4)$	$[MH-CH_3OH]^+$	35 ⎭	

given in Table 3. In addition the elimination of CO from some $[C_8H_7O]^+$ ions isomeric to the primary α-benzoylcarbenium ions a has been studied. The precursor compounds 15–18 are also shown in Scheme 2 and the T_{50} values for CO loss in the 2nd FFR are included in Table 3.

DISCUSSION

Of the two types of α-acylcarbenium ions studied in this paper the reaction of the tertiary α-benzoyl-dimethylcarbenium ion b can be explained in analogy to the behaviour of other tertiary α-acylcarbenium ions.[8] The KER during the elimination of CO from metastable ions b and the corresponding T_{50} values is independent of the mode of preparation of the ion. In fact, $T_{50} = 440 \pm 20$ meV as measured in the CI mass spectra of 2 and 4 agrees well with $T_{50} = 410 \pm 20$ meV obtained previously for ions b generated by electron impact induced dissociation of tertiary butyro-phenone,[8] the small increase in T_{50} probably being due to a reduced energy resolution in the CI mode.[11] The dish-topped peaks observed in the MIKE spectrum of ion b for the elimination of CO and the large value of T_{50} indicate a rearrangement reaction with a large reversed activation energy, and the reaction mechanism shown in Scheme 3 suggests a rearrangement of b via the bridged phenonium ion e as an energy-rich intermediate or transition state.

It has been suggested that the CO loss from the α-acetyldimethylcarbenium ion is preceded by a rearrangement to a more stable hydroxyallyl cation.[12] In the present case the hydroxyallyl cation f (Scheme 3)

is also probably more stable than b. Ion f could have been formed in the CI mass spectra of 2 and 4 by protonation at the carbonyl group followed by a 1,2-elimination of H_2O and CH_3OH, respectively. However, although the increased proton affinity of the α-hydroxyketones compared to monofunctional ketones and alcohols,[9] respectively, indicates strong hydrogen bonding in the $[MH]^+$ ions, the direct formation of ions f by 1,2-elimination of $[MH]^+$ ions can be excluded from the results of labelled derivatives of 2. If present, ions f have to be formed via a 1,4-proton transfer between the terminal methyl groups and the carbonyl group in ion b.[12] The formation of the more stable ions f will slow down the rate of decomposition by increasing the critical energy of the forward reaction, but will have no effect on the KER as long as the phenonium ion e corresponds to the reacting configuration for the loss of CO, which determines the critical energy of the reversed reaction.

It is not clear whether CO elimination and formation of the dimethylbenzyl ion occurs directly from the bridged phenonium ion e or via the dimethylphenyl-acetyl ion d which is formed as a chemically excited species.

The ion d is also formed with low intensity in the CI mass spectrum of 14 and the loss of CO from these metastable ions d gives rise to a rather broad peak and a $T_{50} \approx 250$ meV. The low intensity precludes a peak form analysis in the MIKE spectrum of d. It may be that with increased intensity and increased excess energy in the ions d arising from the rearrangement of b the corresponding signal in the MIKE spectrum is converted into a dish-topped peak as in the case of 2 and 4.
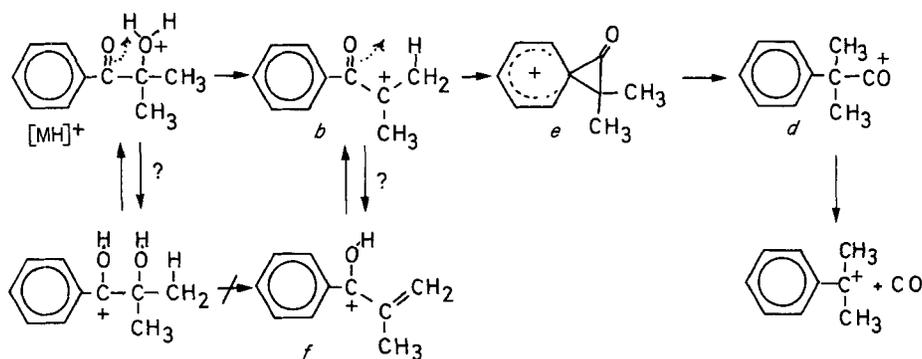
Scheme 3

The elimination of CO from primary α-acylcarbenium ions has not been studied before by metastable ion techniques. This process is known from the EI mass spectra of α-halo-ketones and -esters[13] and gives rise to $[C_7H_7]^+$ ions in the EI mass spectra of ω-halogenoacetophenones. The KER during the loss of CO from metastable ions a in the CI mass spectra of 1 and 3 is quite different from the behaviour of the tertiary ions b. The variation of the peak-shape in the MIKE spectrum of a with the experimental conditions can be attributed either to more than one mechanism contributing to the peak, the relative amount of each process varying with the internal energy and/or the lifetime of the precursor ion(s) or to a special mechanism of the reaction which allows an accumulation of varying amounts of non-fixed energy in the reacting ion without much variation in the reaction rate, i.e. a very shallow rise of the rate with increasing energy of the ion.

The change of instrumental focusing conditions and conditions for collision induced decompositions with the change of CI reagent gas can be excluded as the origin of the variations of the peak shapes for CO loss from ions a. The peak-shapes for the elimination of H_2O and CH_3OH from the $[MH]^+$ ions of 1 and 3, respectively, which precedes the CO loss and which has been measured under the same experimental conditions, are independent of the instrumental conditions.

Besides rearrangement via a three-membered cyclic transition state and an intermediate phenonium ion g the loss of CO from ion a may proceed via the four-membered ring h and subsequent rearrangement to the phenylacetyl ion c or to the o-toluoyl ion i (Scheme 4).

Protonated benzocyclobutenone (15) formed by CI (methane) or CI (isobutane) loses a CO molecule as do the $[M-H]^+$ ions in the 70 eV EI mass spectrum of benzocyclobutenol (16).[18] Loss of CO is also observed
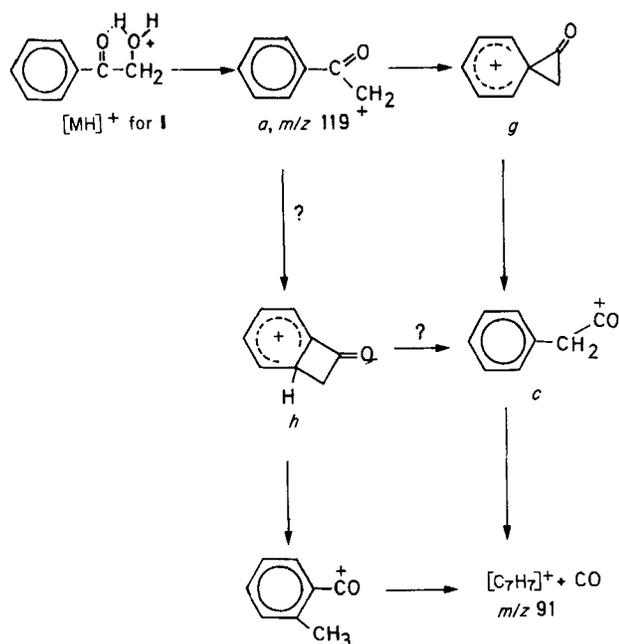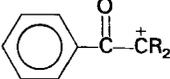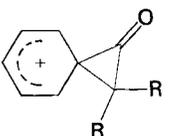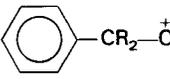

Scheme 4

Table 4. Heats of formation, ΔH_f (kJ mol^{-1}), of ions calculated by MNDO

Ion		R = H	R = CH$_3$
	(a, b)	938	828
	(e, g)	874	849
	(c, d)	764	795
		884	856
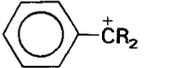
from the o- and m-toluoyl ions generated from the corresponding acids 17 and 18. With the exception of the $[MH]^+$ ions from 15 simple Gaussian peaks are observed for the elimination of CO in the MIKE spectra (Table 3) with T_{50} ranging from 20–35 meV. Obviously, it is not possible to exclude any of these structures from a participation on the CO elimination of the primary α-benzoylcarbenium ion a by the present results, the broad component seen in Fig. 2 arising from CO loss via ions c or $[MH]^+$ ions of 15.

However, none of the $[C_8H_7O]^+$ ions from 13, 15 and 18 showed the significant variation of the KER with the mode of preparation as observed for ions a.

Some characteristic features of the potential energy profile of the rearrangements of ions a and b according to Schemes 3 and 4, respectively, are obtained by a MNDO calculation[14] of the heats of formation, ΔH_f, of the corresponding ions. The results are given in Table 4 and are shown as schematic reaction energy profiles in Fig. 4. It is assumed that the calculations will be at least reliable with respect to the relative ordering of the various species but no experimental values for ΔH_f of the ions a–g are available for a comparison. The $\Delta H_f(e)$ of the bridged phenonium ion is larger than that of the tertiary α-benzoyldimethyl-carbenium ion b and that of the reaction products, the dimethylphenylacetyl ion d or the dimethylbenzyl ion and CO. Hence, the ions b have to cross a potential energy barrier during their rearrangement and decomposition. Furthermore, the variation of the energy with the bond length in the ion e shows that this ion exists in a potential energy well with a critical energy for breaking one of the bonds in the three-membered ring either to ion b or to ion d. Thus, the reversed activation energy is even larger than the 165 kJ mol^{-1} difference between ion e and the reaction products, giving rise to a large KER and the dish-topped peaks observed in the MIKE spectra of ions b.

A large reverse critical energy of similar magnitude is also calculated for the rearrangement of the primary α-benzoylcarbenium ion a. However, in contrast to the tertiary ion b the ion a is the thermochemically least stable species of the reaction sequence. In fact, there
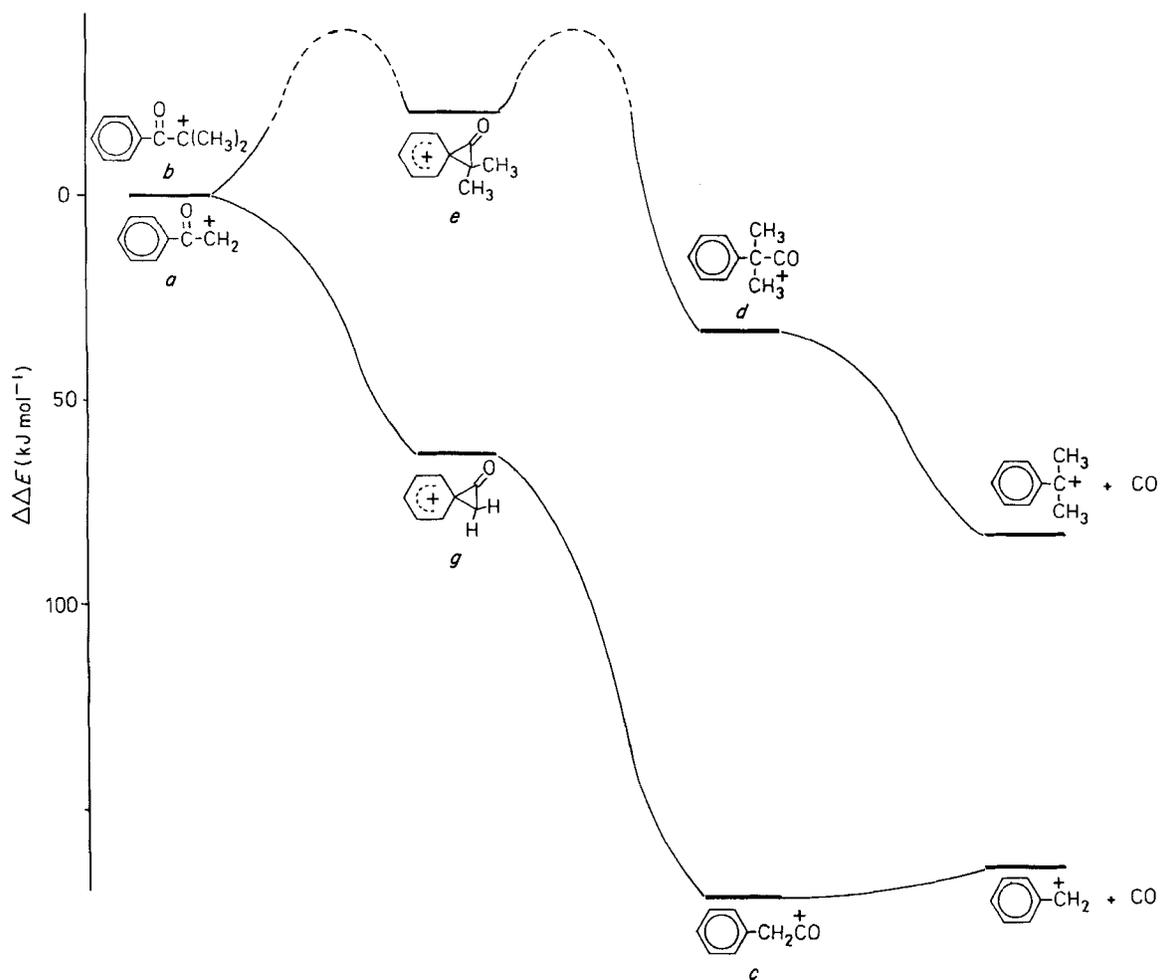
Figure 4. Schematic potential energy profile for the rearrangement of ions *a* and *b*, respectively.

appears to be no potential energy barrier at all between the educt ion *a* and the rearranged phenylacetyl ion *c*, because by starting the MNDO calculation with structure *a* the geometry optimization program automatically converts the system into structure *c*. Therefore, only an approximate value of $\Delta H_f(a)$ could be calculated by keeping the carbenium ion centre in a fixed planar geometry. A reaction energy profile of this type means that the educt ion *a* corresponds also to the very 'early' transition state of the total fragmentation and that only a small fraction of the reverse critical energy should be released during the reaction.[5] Furthermore, the ion *a* should be formed as an unstable species in the CI mass spectra of **1** and **3** by a fast elimination of H_2O and CH_3OH, respectively, and may be observed with some intensity only because of a slow rate of the further decomposition. In contrast to the tertiary ions *b* in the CI mass spectra of **2** and **4** (see Fig. 1), the intensity of the primary ions *a* is rather small in the CI (isobutane) spectra of **1** and **3**. Increasing the energy available for the fragmentation in the CI (methane) spectrum increases the intensities of *a* and its product ion *m/z* 91 only slightly, but favours the formation of benzoyl ions *m/z* 105. Hence, although the reaction sequence $[MH]^+ \rightarrow a \rightarrow$ *m/z* 91 is energetically favoured and the only reaction observed for metastable ions, it is not preferred by

ions with excess internal energy. This indicates that the rate of rearrangement and loss of CO from ions *a* is slow because of entropic effects. Indeed, by rearranging via the bridged phenonium ion g the ion will assume a strained structure, losing thereby every degree of freedom for internal rotations and in addition increasing the frequencies of vibrations at the cyclopropane ring. It is possible that this unusual situation results in a very small 'frequency factor'[15] of the reaction rate.

Usually, ions of a rather narrow band-width of internal energies and of reaction rates are selected by the 'metastable window' from the total distribution of excess energy. A change in this distribution by altering the mode of preparation of the precursor ions will have no large effect on the internal energy but only on the concentration of the metastable ions. This prediction of the QET is borne out by the constant KER for loss of H_2O and CH_3OH from metastable $[MH]^+$ ions (Table 1) and the small variation of the KER during CO elimination from metastable ions *b* (Table 2) under different conditions. An unusual small frequency factor associated with a very slow rise in the rate of the fragmentation with the internal energy of the reacting ion, however, corresponds to a broad 'metastable window'. In this case, a change of the distribution of the excitation energy among the ions

will change not only the relative intensity of metastable ions but also lead to a much broader KER. The calculated energy profile for the rearrangement of the primary α-benzoylcarbenium ions a shows that this is likely the correct explanation for the sensitivity of the KER to the reagent gas used during the chemical ionization and to the reaction time (1st FFR v. 2nd FFR).

EXPERIMENTAL

The ω-hydroxyacetophenones (2-hydroxy-1-aryl-ethanones) 1, 5, 7, 9 and 11 have been synthesized from the corresponding acetophenones by conversion into the trimethylsilyl enol ethers with $(CH_3)_3SiCl/(C_2H_5)_3N$ and oxidation of the trimethylsilyl enol ether with m-chloroperbenzoic acid.[16] The tertiary aryl α-ketols (2-hydroxy-2-methyl-1-aryl-propanones) 2, 6, 8, 10 and 12 were obtained from the corresponding benzaldehydes by addition of trimethylsilyl cyanide to form phenyl trimethylsilyloxyacetonitrils and coupling to acetone in an Umpolung reaction.[17] The O-methyl ethers 3 and 4 were obtained

from the α-ketols 1 and 2 by methylation with CH_3I in the usual manner. All compounds were purified by rectification and characterized by their elemental analysis, their ^1H NMR spectra (Varian EM-60A), IR spectra (Perkin-Elmer 377) and 70 eV EI mass spectra (MAT 311A). The CI mass spectra were obtained with a VG ZAB 2F mass spectrometer by introducing the sample at 150 °C via the septum inlet system and the following standard conditions: electron energy 50 eV, electron emission 0.5 mA, accelerating voltage 6 kV, temperature of the ion source c. 200 °C, pressure in the analysator system 10^{-9} Torr. Isobutane, methane and methanol have been used as reagent gases for the chemical ionization and the pressure of the reagent gas in the ion source has been selected for optimum yield of the $[MH]^+$ ion. Usually the reading on the ion gauge below the ion source housing was between 10^{-5} and 10^{-4} Torr.

Acknowledgements

REFERENCES

1. R. G. Cooks, J. H. Beynon, G. R. Lester and R. M. Caprioli, *Metastable Ions*, Elsevier, Amsterdam (1972).
2. D. H. Williams, *Acc. Chem. Res.* **10**, 280 (1977).
3. J. L. Holmes and J. K. Terlouw, *Org. Mass Spectrom.* **15**, 383 (1980).
4. (a) D. H. Williams, B. J. Stapleton and R. D. Bowen, *Tetrahedron Lett.* 2919 (1978). (b) R. D. Bowen, D. H. Williams and H. Schwarz, *Angew. Chem.* **91**, 484 (1979).
5. (a) B. Schaldach and H. F. Grützmacher, *Int. J. Mass Spectrom. Ion Phys.* **31**, 271 (1979). (b) R. Schubert and H. F. Grützmacher, *J. Am. Chem. Soc.* **102**, 5323 (1980). (c) R. Schubert, D. V. Ramana and H. F. Grützmacher, *Chem. Ber.* **113**, 3758 (1980). (d) H. F. Grützmacher, B. Schaldach, R. Schubert and D. V. Ramana, *Advances in Mass Spectrometry*, Vol. 8, ed. by A. Quayle, p. 795, Heyden, London (1980).
6. J. C. Polyani, *Acc. Chem. Res.* **5**, 161 (1972).
7. (a) A. R. Miller, *J. Am. Chem. Soc.* **100**, 1984 (1978). (b) N. Agmon, *Int. J. Chem. Kinetics* **13**, 333 (1984). (c) J. R. Murdoch, *J. Am. Chem. Soc.* **105**, 2667 (1983).
8. H. F. Grützmacher, A. M. Dommröse and U. Neuert, *Org. Mass Spectrom.* **16**, 279 (1981).
9. D. H. Aue and M. T. Bowers, *Gas Phase Ion Chemistry*, ed. by M. T. Bowers, Vol. 2, Chapt. 9, Academic Press, New York (1979).
10. J. L. Holmes, *Advances in Mass Spectrometry*, Vol. 6, ed. by A. R. West, p. 865, Heyden, London (1974).
11. An increase of T_{50} values measured by CI mass spectrometry and compared to the same reaction induced by

electron impact has been observed in our laboratory also for some other systems; see also Table 3.
12. (a) P. Brown and C. Djerassi, *Tetrahedron* **24**, 2949 (1968). (b) R. G. Cooks, A. N. H. Yeo and D. H. Williams, *Org. Mass Spectrom.* **2**, 985 (1969). (c) G. Bouchoux, Y. Hoppiliard and P. Jaudon, *Tetrahedron Lett.* **23**, 3349 (1982).
13. H. Budzikiewicz, C. Djerassi and D. H. Williams, *Mass Spectrometry of Organic Compounds*, Holden–Day, San Francisco (1967).
14. MNDO: W. Thiel, *QCPE* **4**, 379 (1979).
15. For an introduction to the Quasi-Equilibrium Theory see K. Levsen, *Fundamental Aspects of Organic Mass Spectrometry*, Verlag Chemie, Weinheim (1978).
16. (a) H. House, L. J. Czuba, M. Gall and H. D. Olmstead, *J. Org. Chem.* **34**, 2324 (1969). (b) G. Rubottom, M. A. Vasquez and D. R. Pelegrina, *Tetrahedron Lett.* **49**, 4319 (1974).
17. (a) S. Hünig and G. Wehner, *Synthesis* 522 (1979). (b) K. Deuchert and S. Hünig, *Chem. Ber.* **112**, 2045 (1979). (c) S. Hünig and G. Wehner, *Chem. Ber.* **112**, 2062 (1979).
18. *Note added in proof:* The protonated dimethylcyclobutenone ions isomeric to b have also been investigated. These metastable ions react predominantly by loss of H_2O and can be excluded as intermediates during CO loss from ions b.