# Functional Group Interaction in the Fragmentation of Protonated 2,7-Octanedione

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The fragmentation of 2,7-octanedione, induced by chemical ionization with methane as a reagent gas (CI (CH<sub>4</sub>)), is shown to be extensively governed by the interaction of the two carbonyl groups. Tandem mass spectrometry reveals that a sequential loss of H<sub>2</sub>O and C<sub>2</sub>H<sub>4</sub>O from the  $[M + H]^+$  ion competes with sequential loss of H<sub>2</sub>O and C<sub>2</sub>H<sub>4</sub>O from the  $[M + H]^+$  ion competes with sequential loss of H<sub>2</sub>O and C<sub>6</sub>H<sub>10</sub>, and that both processes occur via the same  $[MH - H_2O]^+$  intermediate. This intermediate is likely to be formed via intramolecular gas-phase aldol condensation and subsequent dehydration. The resulting C(1) protonated 1-acetyl-2-methylcyclopentene structure readily accounts for the observed further decomposition to CH<sub>3</sub>C=O<sup>+</sup> and 1-methylcyclopentene (C<sub>6</sub>H<sub>10</sub>) or, alternatively, to  $[C_6H_9]^+$  (e.g. 1-methylcyclopentenylium) ions and acetaldehyde (C<sub>2</sub>H<sub>4</sub>O). Support for this mechanistic rationale is derived from deuterium isotope labelling and low-energy collision-induced dissociation (CID) of the  $[MH - H_2O]^+$  ion. The common intermediate shows a CID behaviour indistinguishable by these techniques from that of reference ions, which are produced by gas-phase protonation of the authentic cyclic aldol or by gas-phase addition of an acetyl cation to 1-methylcyclopentene in a CI (CH<sub>3</sub>COOCH<sub>3</sub>) experiment.

# INTRODUCTION

Neighbouring group participation in the fragmentation of molecules with more than one functional group has attracted early attention<sup>1</sup> in mass spectrometry because of special effects on ion formation, which are relevant both to structural assignment and the basic understanding of gas-phase ion chemistry. In the present study, effects of increasing functional group separation on the fragmentation of  $[M + H]^+$  ions, which were generated by chemical ionization with methane as reagent gas (CI (CH<sub>4</sub>)), were investigated for a series of aliphatic diketones CH<sub>3</sub>CO(CH<sub>2</sub>)<sub>n</sub>COCH<sub>3</sub>. Figure 1 shows the relative abundances (% TIC) of selected ions as a function of *n*. The  $[M + H]^+$  ions, for instance, display a broad stability minimum between n = 2 and n = 6. This behaviour is mirrored by a broad stability maximum for the  $[MH - H_2O]^+$  ions, which may reflect the operation of different modes of elimination depending on chain length (e.g. the formation of protonated furans has been reported in previous work<sup>2</sup> for the case n = 2). For another important fragment, which arises from the combined loss of H<sub>2</sub>O and a C<sub>2</sub>H<sub>4</sub>O neutral, the maximum of ion abundance is comparatively narrow, i.e. limited essentially to the three members of the series with n = 4, 5 and 6. This type of profile indicates a highly specific mode of interaction between the two carbonyls via five-, six- and seven-membered cyclic transition states and/or intermediates, which renders this process attractive for a detailed study of cooperative effects. The maximum weight of this process in protonated 2,7-octanedione (1; n = 4; interaction probably via five-membered cyclic structures) makes this particular homologue the compound of choice.

## **EXPERIMENTAL**

To secure identical CI conditions for all homologues of comparative series this study, gas the in chromatography/mass spectrometry (GC/MS) analysis of an artificial equimolar mixture was performed using a Finnigan 4000 mass spectrometer. The instrument was coupled with a Carlo Erba 4160 Fractovap gas chromatograph as previously described.<sup>3</sup> Typical analyses were performed in the CI (CH<sub>4</sub>) mode (0.4 mbar reagent gas pressure) by on-column sample injection on glass capillary columns ( $20 \text{ m} \times 0.3 \text{ mm}$ , SE-54 coating, 5 °C min<sup>-1</sup> temperature programming over a range of 50–250 °C, He carrier gas).

Tandem mass spectrometry (MS/MS) was performed on a Finnigan MAT TSQ 45 triple-stage quadrupole (QQQ) mass spectrometer under a variety of CI conditions (CI (CH<sub>4</sub>), CI (i-C<sub>4</sub>H<sub>10</sub>), CI (CH<sub>3</sub>COOCH<sub>3</sub>)). To establish CI (CH<sub>3</sub>COOCH<sub>3</sub>) conditions, ~0.35 mbar reagent gas was supplied to the ion source from a heated reservoir<sup>3</sup> (250  $\mu$ A emission current, 15 eV ionizing energy). Batch inlet system introduction was used for most samples, which allowed averaging of scans for improved precision. Collision-induced dissociation (CID) spectra were obtained by adjusting collision energy (Q<sub>2</sub> offset voltage) and collision gas (argon) pressure to the stated values. For reactive collisions in Q<sub>2</sub>, a steady flux of slow CH<sub>3</sub>C $\equiv$ O<sup>+</sup> ions (4.8 eV kinetic energy, mass selection by Q<sub>1</sub>) was produced from

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**Figure 1.** Relative abundances of  $[M + H]^+$ ,  $[M + H - H_2O]^+$  and  $[M + H - H_2O - C_2H_4O]^+$  ions in Cl (CH<sub>4</sub>) of aliphatic diketones CH<sub>3</sub>CO(CH<sub>2</sub>)<sub>n</sub>COCH<sub>3</sub> as a function of carbonyl group separation (n).

methyl acetate under 15 eV (nominal) electron impact (EI) conditions. 1-Methylcyclopentene and its deuterated analogues  $(\alpha-d_3, 2,5,5-d_3 \text{ and } 3,3,4,4-d_4)$ , which provided the reactive target gases, were supplied to  $Q_2$ from a heatable liquid reagent reservoir. To compensate for these (15 eV) low-sensitivity conditions, profile data were evaluated  $(10 \text{ u s}^{-1}, \text{ average of } 300 \text{ scans})$ . To permit GC-MS/MS analyses of crude reaction mixtures (e.g. 2,7-octanedione containing 1-acetyl-2-methylcyclopentene together with the cyclic reference aldol 1hydroxyl-1-methyl-2-acetylcyclopentane after prolonged storage in  $CH_2Cl_2$  solution) the QQQ instrument was also coupled with a Carlo Erba 4160 Fractovap gas chromatograph, as described in Ref. 3. Diketones that were commercially not available were prepared according to a general synthetic route<sup>4</sup> which involves a sequence of simultaneous chain extensions on both termini:

$$(CH_{2})_{n-2}Br_{2} \xrightarrow{CH_{2}(COOEt)_{2}} (CH_{2})_{n-2}[CH(COOEt)_{2}]_{2}$$

$$\xrightarrow{H_{3}O^{+}} (CH_{2})_{n}[COOH]_{2} \xrightarrow{SOCI_{2}} (CH_{2})_{n}[COCI]_{2}$$

$$\xrightarrow{CH_{2}N_{2}} (CH_{2})_{n}[COCHN_{2}]_{2} \xrightarrow{HI} (CH_{2})_{n}[COCH_{2}I]_{2}$$

$$\xrightarrow{Zn/AcOH} (CH_{2})_{n}[COCH_{3}]_{2}$$

With  $BrCD_2CD_2Br$  used as the starting material, 4,4,5, 5- $d_4$ -2,7-octanedione (1a) was obtained in the same manner.

Attempts to convert 1 to its cyclic aldol 1-hydroxyl-1methyl-2-acetylcyclopentane (2) under mild acid or base catalysis invariably yielded the conjugated cyclic enone 1-acetyl-2-methylcyclopentene (4).<sup>4</sup> On prolonged storage of 1 in CH<sub>2</sub>Cl<sub>2</sub> solution, 2 and 4 were formed, however, as minor constituents (bulk of unreacted 1), which could be easily separated in GC-MS and GC-MS/MS experiments. The deuterium-labelled 1-methylcyclopentenes (3,3,4,4-d<sub>4</sub>-, 2,5,5-d<sub>3</sub>- and  $\alpha$ -d<sub>3</sub> analogues), required as additional reference materials, were obtained by Grignard reaction and subsequent dehydration, using CH<sub>3</sub>I (or CD<sub>3</sub>I) and cyclopentanone (or its 3,3,4,4-d<sub>4</sub>- or 2,2,5,5-d<sub>4</sub> analogues) as the respective starting materials.<sup>4</sup>

# **RESULTS AND DISCUSSION**

As evident from Fig. 1, the CI (CH<sub>4</sub>) spectrum of the model compound 2,7-octanedione 1 (Fig. 2) is dominated by two fragment ions  $a (m/z \ 125)$  and  $b (m/z \ 81)$ , which can be plausibly assumed to arise from loss of H<sub>2</sub>O and H<sub>2</sub>O/C<sub>2</sub>H<sub>4</sub>O, respectively. Less prominent ions correspond to elimination of C<sub>3</sub>H<sub>6</sub>O (acetone,  $m/z \ 85$ ) and, more surprisingly, of C<sub>2</sub>H<sub>4</sub>O<sub>2</sub> (acetic acid,  $m/z \ 83$ ; cf. also protonated acetic acid at  $m/z \ 61$ ).

The two-step genesis of ion b by a sequential loss of  $H_2O$  and  $C_2H_4O$  (acetaldehyde) from  $[M + H]^+$  is readily verified by MS/MS. Daughter experiments allow the 'resolution' of fragmentation channels by the mass-





Figure 3. Low-energy CID spectra of  $[M + H]^+$  ions of 2,7-octanedione (1, m/z 143; 10 eV collision energy; 1.3 mbar argon collision gas, indicated) and  $[M + H - H_2O]^+$  intermediate (*a*, m/z125; 20 eV collision energy; 0.8 mbar argon collision gas, indicated).

selection of long-lived educt ions and the study of their decomposition by CID. The implicated analogy between CID and unimolecular fragmentation in the ion source relies, of course, on the retention of the original structures by the long-lived educt ions. As the CID spectra of  $[M + H]^+$  and  $[MH - H_2O]^+$  (Fig. 3; m/z 143 and 125, respectively) represent 'subspectra' of the complete CI spectrum (Fig. 2), this important criterion appears to be met. The assumed intermediacy of a

becomes especially evident when, under CID conditions, mass-selected m/z 125 parent ions display a pronounced daughter ion signal for ion b (m/z 81, Fig. 3).

Selection of specific parent ion species eliminates contributions from reagent ions which would otherwise obscure the low-mass region of the spectrum (Fig. 2, m/z < 60). Thus, an additional major daughter ion c(m/z 43) is detected in the fragmentation of the [MH  $- H_2O]^+$  intermediate as a major competitor of b. An elemental composition of  $C_2H_3O$  (in the simplest case<sup>5</sup> the acetyl cation  $CH_3C\equiv O^+$ ) indicates c to be the ionic counterpart of the  $C_2H_4O$  neutral lost in the genesis of b.

On the basis of this evidence (five-membered cyclic structures; two-step genesis of b and c from  $[M + H]^+$  with expulsion of a terminal CH<sub>3</sub>CO moiety both as neutral and cationic species) the mechanistic rationale shown in Scheme 1 is proposed.

Gas-phase rearrangement of  $[M + H]^+$  ions prior to dissociation is thought to occur via enolization of the protonated keto function and intramolecular aldol condensation (an intermolecular variety has been reported previously<sup>6</sup>). Subsequent (6-centre) proton migration from the keto to the hydroxyl function in the cyclic product  $([M + H]^+$  ion of the aldol 2) produces an excellent leaving group for the elimination of H<sub>2</sub>O. The resulting tertiary  $\beta$ -ketocarbenium ion (intermediate a, m/z 125), is structurally predestined for further facile decomposition by  $\beta$ -cleavage,<sup>7</sup> yielding neutral 1-methylcyclopentene (3) along with ion c (m/z 43;  $CH_3C \equiv O^+$  and possibly isomers thereof<sup>5</sup>). In competition with this 'direct' bond cleavage, a ions may also decompose by rearrangement within a long-lived iondipole complex.<sup>8</sup> In this case, initially formed c ions may abstract a hydride ion from a favourable site in the polarizable neutral (e.g. the allylic 3-position) and thus



produce the 1-methylcyclopentenylium ion  $b (m/z \ 81)$  together with acetaldehyde. Transprotonation within this second ion-dipole complex may finally produce the low-abundance ion  $d (m/z \ 45)$ . It is interesting to note that the initial processes closely parallel the condensed-phase chemistry of 1, i.e. aldol condensation to 2 (cf. Experimental), followed by dehydration to 4 as the major product.<sup>9</sup> Formation of 2 from 1 prior to ionization is ruled out on the basis of distinctly different chromatographic behaviour and the CID spectra of  $[M + H]^+$  ions (not shown).

The large exothermicity of the initial protonation of 1  $CH_5^+$  (standard reaction enthalpy at least by  $-285 \text{ kJ mol}^{-1}$ , i.e. without internal hydrogen bonding) renders the whole sequence of gas-phase reactions thermochemically favourable. Whereas the  $\beta$ -cleavage step is moderately endothermic, the conversion of the second ion/neutral first into the fragment  $(CH_3C \equiv O^+/1\text{-methylcyclopentene} \rightarrow [C_6H_9]^+/$ pair  $CH_3CH=O$ is practically thermoneutral  $(< -10 \text{ kJ mol}^{-1})$ . The formation of ion d (together with 1-methylcyclopentadiene) would again be moderately endothermic ( $\sim +40 \text{ kJ mol}^{-1}$ ).

To test this mechanistic rationale, especially with respect to the regiospecificity of individual steps, 4,4,5,5tetradeuterio-2,7-octanedione (1a) was subjected to analogous GC-MS/MS experiments. When mass-selected by  $Q_1$  for CID,  $[M + H]^+$  ions  $(m/z \ 147 \ in \ 1a)$  lose HOH exclusively, i.e. give a single signal at m/z 129 for the a intermediate (Fig. 4) in close agreement with the  $[M + H]^+$  fraction decomposing in the ion source (full spectrum, not shown). CID of the  $[MH - H_2O]^+$  intermediate  $a-d_4$  (m/z 129, Fig. 4) shows an unshifted c ion at m/z 43, as required by the proposed scheme. Also in accordance with this scheme, the major fraction (about 2/3) of ion b is shifted to m/z 84 due to abstraction of D<sup>-</sup> from the allylic 3- (or, less likely, the 'homoallylic' 4-) position (cf. Ref. 10). The remaining fraction (about 1/3) of b is shifted to m/z 85, and is probably due to H<sup>-</sup>



**Figure 4.** Low-energy CID spectra of  $[M + H]^+$  ions of 4,4,5,5-tetradeuterio-2,7-octanedione (**1a**, m/z 147; 10 eV collision energy; 1.3 mbar argon collision gas, indicated) and  $[M + H - H_2O]^+$  intermediate ( $a-d_4$ , m/z 129; 20 eV collision energy; 0.8 mbar argon collision gas, indicated).

abstraction from the other allylic sites, i.e. the 5- and/or the exocyclic  $\alpha$ -CH<sub>3</sub> position. This approximate 2:1 intensity ratio in favour of abstraction from the 3position prevails over the entire range of available collision energies (0-30 eV). This may indicate the operation of one (regioselective) mode of CH<sub>3</sub>CH=O elimination rather than of two (or more) independent routes.

The formation of ions b (e.g.  $b-d_3$  and  $b-d_4$ ; m/z 84 and 85) and c (m/z 43) from a common intermediate a is also supported by pseudo-breakdown curves (Fig. 5) of the respective precursors ( $[M(d_4) + H]^+$ , m/z 147;  $a-d_4$ , m/z 129). The rise of relative abundance of c v. b with increasing collision energy implies different modes of formation by direct cleavage and rearrangement, respectively. It is especially sharp (1:1 c:a ratio at about 9.5 eV) in the case of direct formation from  $a-d_4$  (lower trace). In the case of two-step formation of b and c from  $[M + H]^+$  these effects are naturally less pronounced (upper trace).

Evidence for the intermediacy of the 'first' ion-dipole complex comes from similar regioselectivities, which can be observed when  $CH_3C\equiv O^+$  is directly reacted with the inferred neutral, 1-methylcyclopentene (3). These ion-molecule reactions were carried out in  $Q_2$  with 3 and its deuterated analogous serving as target gases in reactive low-energy collisions (4.8 eV collision energy, collision gas pressures about 1.6 mbar) with massselected  $CH_3C\equiv O^+$ . The required  $CH_3C\equiv O^+$  ions of high purity were generated according to the literature<sup>5</sup> from methyl acetate by the use of 15 eV electrons. The



**Figure 5.** Pseudo-breakdown curves (major daughter ions) of  $[M + H]^+$  and  $[M + H - H_2O]^+$  ions of 4,4,5,5-tetradeuterio-2,7-octanedione (**1a**; 5–20 eV collision energy; 1.1 mbar krypton collision gas, indicated).





**Figure 6.** Partial daughter ion spectra (profile data) obtained from reactive collisions of  $CH_3C\equiv 0^+$  with (a) 1-methylcyclopentene (3), (b) 1-(trideuteriomethyl)cyclopentene (3c), (c) 3,3,4,4-(tetradeuterio)-1-methylcyclopentene (3a) and (d) 2,5,5-(trideuterio)-1-methylcyclopentene (3b) in  $\Omega_2$ . Collision condition: 4.8 eV collision energy; about 1.6 mbar target gas pressure, indicated.

analysis of 3,3,4,4- $d_4$ -, 2,5,5- $d_3$ - and  $\alpha$ - $d_3$  analogues (3a, 3b and 3c, respectively) under these conditions shows that the  $[M - H]^+$  ions arise practically exclusively from H<sup>-</sup> abstractions at two allylic (and possibly one homoallylic) sites (Fig. 6). The low abundance of m/z 67 (major fragment ion in EI mass spectrometry) indicates that 'foreign' contributions to  $[M - H]^+$  by loss of H' from M<sup>+</sup> (produced by charge exchange) are negligible. The proportions of about 67% and 33% of H<sup>-</sup> abstraction from the 3- (or 4-) and 5-positions, respectively, are in full agreement with the 67% (3- or 4position) and 33% (sum of 5- and  $\alpha$ -positions) observed for 1a (both CID and conventional spectrum). The close fit of the regioselectivities and the substantial abstraction of H<sup>-</sup> from the allylic 5-position lend support to the intermediacy of an ion-dipole complex since the geometry of the covalent adduct a renders direct hydrogen transfer from this 'remote' site to the 2-acetyl substituent highly unlikely.

Apart from establishing ion 'genealogy', low-energy CID was also employed in an attempt to characterize ion structures proposed in Scheme 1. Proof of the fivemembered ring structure for ion b (1-methylcyclopentenylium ion, m/z 81) as one of the 'final' products would have supported the proposed specific interaction in the cyclization step, but was inconclusive in this case. Good agreement between the CID spectrum of ion b (m/z 81, 30 eV, Kr target gas) and that of  $[M - H]^+$ reference ions from 1-methylcyclopentene (3, subjected to isobutane CI) was obtained, but provided insufficient evidence for structural identity in the light of an earlier high-energy CID study on isomeric  $[C_6H_9]^+$  ions prepared from 13 cyclic and linear precursors. These ions had been found to be indistinguishable because of





**Figure 7.** Low-energy CID spectra of m/z 125 ions generated from (a) 2,7-octanedione (1,  $[M + H - H_2O]^+$ ), (b) 1-hydroxyl-1-methyl-2-acetylcyclopentane (2,  $[M + H - H_2O]^+$ ), (c) 1-methylcyclopentene (3,  $[M + CH_3C \equiv O]^+$ ), (d) 1-acetyl-2-methylcyclopentene (4,  $[M + H]^+$ ) and (e) cyclohexene (5,  $[M + CH_3C \equiv O]^+$ ). Collision conditions: 20 eV collision energy; 0.8 mbar argon collision gas, indicated.

rearrangement to the stable 1-methylcyclopentenylium ion as the common final product.<sup>11</sup>

The structure of the 'educt' rather than the product ion, i.e. the  $[MH - H_2O]^+$  intermediate *a*, would be even more relevant in the present context, as it represents a species mechanistically 'closer' to the point of functional group interaction on the reaction coordinate. The 2-acetyl-1-methylcyclopentylium reference ion required for this analysis was prepared via two independent routes (cf. Scheme 2). The most obvious genesis relied on the dehydration of the gas-phase protonated cyclic aldol 2, which was formed in a solution of 1 as a minor constituent together with the conjugated enone dehydration product, 1-acetyl-2-methylcyclopentene (4). Direct gas-phase protonation of 2 as the conjugate base of the first cyclic, i.e. crucial intermediate, provides a short cut of the reaction sequence at a stage at which the actual cyclization, for which evidence is primarily sought, has already occurred. An alternative, direct access to the reference ion *a* was attempted via reversal of the fragmentation process under discussion, i.e. by formation of an adduct ion of  $CH_3C \equiv O^+$  with neutral 1-methylcyclopentene (3, cf. Scheme 2). High regioselectivity in favour of reaction at C(2) was expected for this process. The ionic educt for this ion-molecule reaction, now carried out in the ion source rather than in  $Q_2$ , was prepared by methyl acetate CI (15 eV electron energy in analogy to the EI genesis of  $CH_3C\equiv O^+$ ). It was assumed that high purity of the acylating species (predominantly  $[CH_3COOCH_3 + CH_3CO]^+$  according to reagent ion monitoring) was attained under these conditions.

For MS/MS analyses, mass-selected a ions  $(m/z \ 125)$ from the diketone (1, methyl acetate CI, batch introduction),  $[MH - H_2O]^+$  ions from the cyclic aldol (2, methyl acetate CI, GC-MS/MS experiment), and [M  $+ CH_3CO]^+$  ions from 1-methylcyclopentene (3, methyl acetate CI, batch introduction) were subjected to CID in successive experiments without changing the collision conditions (Fig. 7). Good agreement between the three spectra was indeed obtained when m/z 75 (protonated CH<sub>3</sub>COOCH<sub>3</sub> due to minor leakage of the CI reagent gas into  $Q_2$ ) was excluded from the comparison. By contrast, the CID spectrum of another potential reference ion, protonated 1-acetyl-2-methylcyclopentene (4, methyl acetate CI, GC-MS/MS analysis) differs markedly from the above spectra (cf. m/z 45, 91, 107). The enhanced stability of the  $[M + H]^+$  ions of 4 is likely to be due to preferential protonation at the carbonyl oxygen. Rapid interconversion of the Oprotonated enone structure into that of ion a via a 1,3

proton shift can therefore be excluded. Cyclohexene (5) was included in the comparison as an important cyclic isomer of 3, in order to ascertain whether at least part of the cycloalkene/CH<sub>3</sub>C $\equiv$ O<sup>+</sup> adducts retain the structural integrity required for distinction. Significant spectral differences between Fig. 7, trace e v. Fig. 7, traces a-c (e.g. m/z 45; m/z 71, due to loss of butadiene?) suggest that the originally formed 2-acetyl-1-methylcyclopentylium and 2-acetylcyclohexylium ions do not (completely) interconvert under these experimental conditions (in contrast to the complete rearrangement reported for the unsubstituted cyclohexylium to the methylcyclopentylium ion in high-energy CID<sup>12</sup>). These CID results, together with the practically identical regioselectivities of hydride abstraction reactions in the formation of intermediates from different precursors, strongly support the functional group interaction via gas-phase aldol condensation and the subsequent decomposition via the ion-dipole complexes proposed in the mechanistic scheme.

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