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The unexpected decarbonylation of ionized 2,3-pentanedione and related diketones

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Dedicated to the memory of Chava Lifshitz, a truly dedicated scientist and a good friend.

Abstract

The fragmentation of the 2,3-pentanedione radical cation gives rise to an unexpected composite metastable ion peak, *m*/*z* 72, resulting from the isobaric losses of CO and C_2H_4. These two fragmentation channels are energetically competitive (i.e., the transition states have similar energies). The two processes yield $[CH_3C(O)CH_2CH_3]^{\bullet+}$ and $[CH_3C(OH){=}C{=}O]^{\bullet+}$, respectively. The latter new ion, which is produced by a McLafferty rearrangement, has $\Delta_f H^\circ = 604$ kJ/mol, obtained from G3 calculations. The four competing processes for metastable $[CH_3COCOCH_2CH_3]^{\bullet+}$, the (intense) losses of $CH_3CO^\bullet$, $CH_3CH_2CO^\bullet$ and the weak losses of C_2H_4 and CO and their transition states were placed on a potential energy surface computed at the G3 level of theory. The homologous ionized diketone 2,3-butanedione also displays the decarbonylation channel and 3,4-hexanedione loses CO and C_2H_4.

Keywords: Diketones; McLafferty rearrangement; Decarbonylation; Structure; Mechanism

1. Introduction

Among the most thoroughly studied organic cation dissociations is the very well known "McLafferty Rearrangement" [1–3]. This reaction is common to almost all aliphatic aldehydes, ketones, carboxylic acids, esters, amides, etc., and it requires the presence of at least one H-atom attached to the atom at the position-γ to the CO group [4]. The smallest diketone that could display a McLafferty rearrangement is 2,3-pentanedione. This would involve the loss of an ethene molecule, $(M\text{-}28)^{\bullet+}$, as shown in Scheme 1.

Very recently, Kercher et al. [5] determined the 298 K heats of formation ($\Delta_f H^\circ$) of the propanoyl ion and radical and of ionized 2,3-pentanedione itself by the technique of threshold photoelectron photoion coincidence (TPEPICO) spectroscopy. This simple bond cleavage wholly dominated their observations and under their experimental conditions there was no evidence for the participation of any McLafferty rearrangement. In this paper we report the metastable ion (MI) and collision induced dissociation behavior of this diketone and also the homologues 2,3-butanedione and 3,4-hexanedione. These three compounds are pale yellow liquids and are used as flavoring agents to give a pleasant taste and a sweet odor to a variety of foods, such as margarine, candies and some beers [6].

Gas phase radical cations with low internal energy often dissociate via rearrangement processes in the metastable ion time-frame. The typical flight-time of a metastable ion in a sector mass spectrometer is 10^{-4} to 10^{-6} s during which they decompose in a field-free region of the instrument [7,8]. In this study, the 2,3-pentanedione radical cation was observed to undergo a McLafferty rearrangement in the MI time-frame, but unexpectedly giving a composite peak. As will be described below, this arises because CO loss competes with the ethene loss and therefore it was deemed to be of interest to investigate the behaviors of the closest homologues, 2,3-butanedione and 3,4-hexanedione. With the aid of computational chemistry, a complete potential energy surface for the fragmentations of ionized 2,3-pentanedione was constructed.

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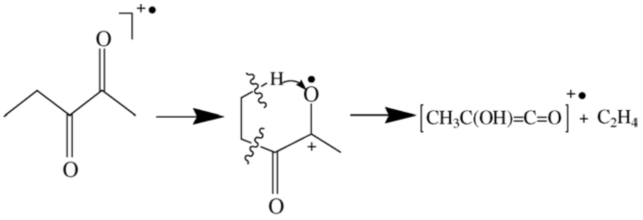


Scheme 1. The McLafferty rearrangement of ionized 2,3-pentanedione leading to the loss of C_2H_4.

2. Experimental and theoretical

All experiments were carried out on a modified VG-ZAB tandem mass spectrometer [9] with BEE geometry (VG Analytical, Manchester, UK). Metastable ion and collision-induced dissociation (CID) mass spectra of the ionized diketone molecules were observed in the second field-free region (2FFR) of the mass spectrometer. The ion accelerating voltage was 8 kV. Helium was used as the collision gas for the CID experiments. The fragment ions generated in the 2FFR from the mass selected ionized diketones were energy selected by the first electrostatic analyzer and transmitted into the 3FFR to study their MI and CID characteristics to aid their structure identification. All spectra were recorded with the ZABCAT program developed by Mommers Technologies [9].

The ionized molecules were generated in a low pressure ion source [10] by 70 eV electron impact ionization. Liquid samples were introduced into the source via a liquid septum inlet. The compounds $CH_3CH_2COCOCH_2CH_3$, $CH_3CH_2COCOCH_3$, $CH_3COCOCH_3$, $CH_3CH_2COCH_3$ and CH_3COCH_3 were of research grade and were purchased from Aldrich and were used without further purification.

The Gaussian 98 programs [11] were used to perform standard ab initio molecular orbital calculations to investigate the potential energy surface (PES). Optimized geometries and the energies of all minima and transition states were calculated at the B3LYP/6-31+G(d) level of theory. Zero point energies obtained from calculations of vibrational frequencies at the same level of theory were scaled by a factor of 0.9806 [12]. A single point energy calculation at the G3 level of theory on the optimized ion structures at B3-LYP/6-31+G(d) was applied to obtain accurate relative energies and also the heat of formation of the new ion, $CH_3C(OH){=}C{=}O^{\bullet+}$, resulting from the loss of ethene from ionized 2,3-pentanedione.

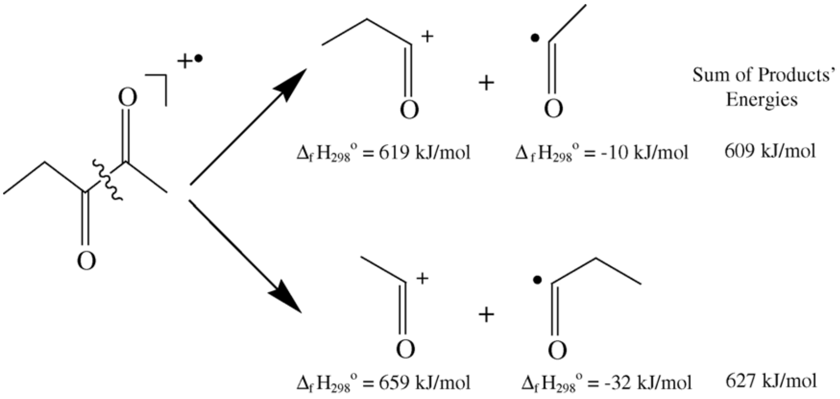
3. Results and discussion

3.1. The 2,3-pentanedione radical cation

3.1.1. The MI and CID mass spectra of ionized 2,3-pentanedione

There are two competing dissociations, as shown in Scheme 2, arising from the cleavage of the 2,3 C–C bond, the weakest bond in the radical cation, leading to the formation of the propanoyl ion (m/z 57) and an acetyl radical and the generation of the acetyl cation (m/z 43) and a propanoyl radical. The enthalpy values for CH_3CO^+ and $CH_3CO^\bullet$ have been determined by Fogleman et al. [13] as $\Delta_f H^\circ\,[CH_3CO^+] = 659$ kJ/mol (very close to the earlier result of Traeger et al., 656 kJ/mol [14]) and $\Delta_f H^\circ\,[CH_3CO^\bullet] = -10$ kJ/mol [15]. The heat of formation of the $C_2H_5CO^+$ ion has been recently measured as 619 kJ/mol by Kercher et al. [5], in very good agreement with Harvey and Traeger's value of 617.8 ± 0.9 kJ/mol [16]. The product energies given in Scheme 2 show that the first dissociation channel (to produce the $C_2H_5CO^+$ ion) is energetically more favorable than the second (to yield the CH_3CO^+ ion) by ca. 18 kJ/mol. Thus, in the metastable ion mass spectrum of ionized 2,3-pentanedione (Fig. 1A) the base peak is m/z 57, i.e., the propanoyl ion, with a much weaker signal corresponding to the acetyl ion (m/z 43), only ca. 3% of m/z 57. Kercher et al. could not measure a threshold for m/z 43. Because these ions arise from a simple 2,3 C–C bond cleavage, the collision-induced dissociation mass spectrum of ionized 2,3-pentanedione (Fig. 1B) showed that the peaks for $C_2H_5CO^+$ and CH_3CO^+ are both strongly sensitive to collision gas.

The MI mass spectrum however also shows a small composite peak corresponding to m/z 72 (ca. 1.6% of m/z 57), the loss of 28 mass units from the ionized diketone. It is expected to arise from the McLafferty rearrangement of the molecular ion, leading to C_2H_4 loss. This MI peak was wholly insensitive to collision gas signifying that the mass selected precursor ion has undergone rearrangement prior to this fragmentation [17]. The



Scheme 2. The simple bond dissociation paths of ionized 2,3-pentanedione.

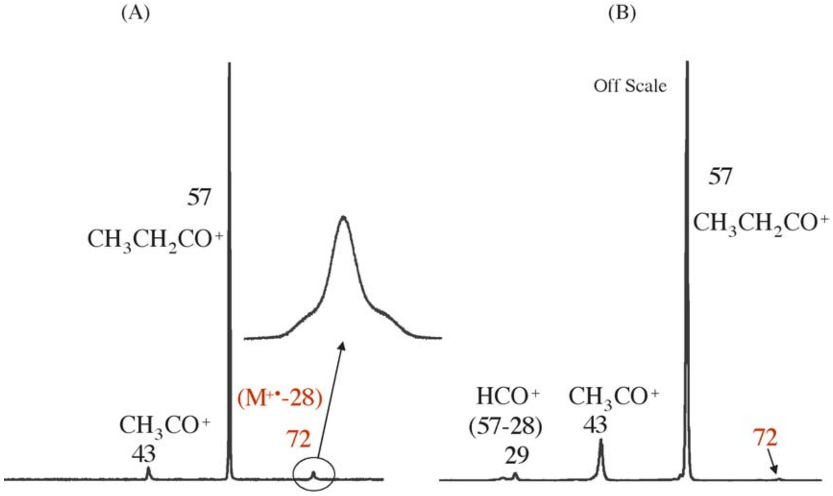


Fig. 1. (A) Metastable ion (MI) and (B) collision-induced dissociation (CID) mass spectra of ionized 2,3-pentanedione.

composite peak consists of a large kinetic energy release (KER) component, giving rise to the broad base and a small KER component at the peak's center (Fig. 1). This could result from the metastable ion undergoing two competing dissociations to give fragment ions of different structures [7] or less likely, from two transition states leading to a single product ion. The structure of each component of the composite peak was identified as follows. Slices of this peak (from the edge or at the center) were transmitted by the electrostatic analyzer into the third field-free region (3FFR), where the CID characteristics of the ions in these slices were recorded. The CID mass spectrum of each component of the $(M\text{-}28)^{\bullet+}$ peak is shown in Fig. 2. That of the large kinetic energy release component produced two major fragment ions (m/z 43 and 57), as shown in Fig. 2B. This CID mass spectrum is identical to that of ionized 2-butanone (Fig. 2C), showing that the large KER component arises from the loss of CO from a rearranged ionized 2,3-pentanedione. The large kinetic energy release indicates that the reaction has a significant reverse energy barrier [7]. This dissociation thus requires a rearrangement of the 2,3-pentanedione ion to an isomeric species, over an energy barrier that is higher than that of the thermochemical dissociation limit for the decarbonylation reaction. The reaction path includes the stable state and transition state structures that are shown in the potential energy surface for ionized 2,3-pentanedione (see Fig. 3). The loss of a CO molecule is commonly observed in the (MI) mass spectra of ionized esters [18], phenols [19], dimethyl phosphonates [20], acetamides [21] and diketones [22]. In all the above systems, the low-energy (metastable) ion undergoes decarbonylation via a rearrangement process and so in the present example the hidden mechanism of the decarbonylation is worth discovering. Although such rearrangements involve an energy barrier, the production of the low energy CO molecule ($\Delta_f H^\circ(CO) = -110.53$ kJ/mol [23]) makes the decarbonylation reaction able to compete with other fragmentation processes.

The center of the $(M\text{-}28)^{\bullet+}$ ion peak contains fragments resulting from both components, i.e., it is contaminated by some ionized 2-butanone (the broad component). However, the CID mass spectrum contains an intense signal at m/z 44 which does not appear in the CID mass spectrum of the 2-butanone ion and so must arise from the dissociation of the center ion structure. The 2,3-pentanedione ion contains a carbonyl group (at atom 2) that can accept a γ-hydrogen from the ethyl group via a McLafferty rearrangement. The product ion is a hydroxyl-substituted methylketene. The computations showed that this 1,5-H transfer process leads to an intermediate (structure III in Fig. 4) which can lose ethene by cleavage of the α–β bond in ion (III) and the detailed mechanism is described in the section below.

3.1.2. The potential energy surface of ionized 2,3-pentanedione

Calculations at the G3//B3-LYP level of theory were performed to produce a PES for ionized 2,3-pentanedione. Also investigated were the mechanisms of the isomerizations for the losses of CO and C_2H_4. The energies (in kJ/mol) shown on the PES are relative to the calculated energy of the global minimum I of ionized 2,3-pentanedione, obtained at the B3LYP/6-31+G(d) and G3 level of theories, and are given in Table 1. The 0 K potential energy profile is shown in Fig. 3.

The ground state of ionized 2,3-pentanedione is a loosely C_2–C_3 bonded species (see in Fig. 4, the geometry of ion I).

Table 1
Calculated relative energies, E_{rel} (in kJ/mol), at 0 K for the different structures obtained from B3-LYP/6-31+G(d) and G3 levels of theory

Structures	B3-LYP/6-31+G(d) E_{rel} (0 K)	G3 E_{rel} (0 K)
I	0	0
II	5	4
III	114	98
IV	50	38
TS1	142	128
TS2	5	6
TS3	108	102
$CH_3CH_2CO^+ + CH_3CO^\bullet$	106	99
$CH_3CH_2CO^\bullet + CH_3CO^+$	129	119
$CH_3CH_2C^{\bullet+}(=O)CH_3 + CO$	62	57
$CH_3C^{\bullet+}(OH)CO + C_2H_4$	163	127

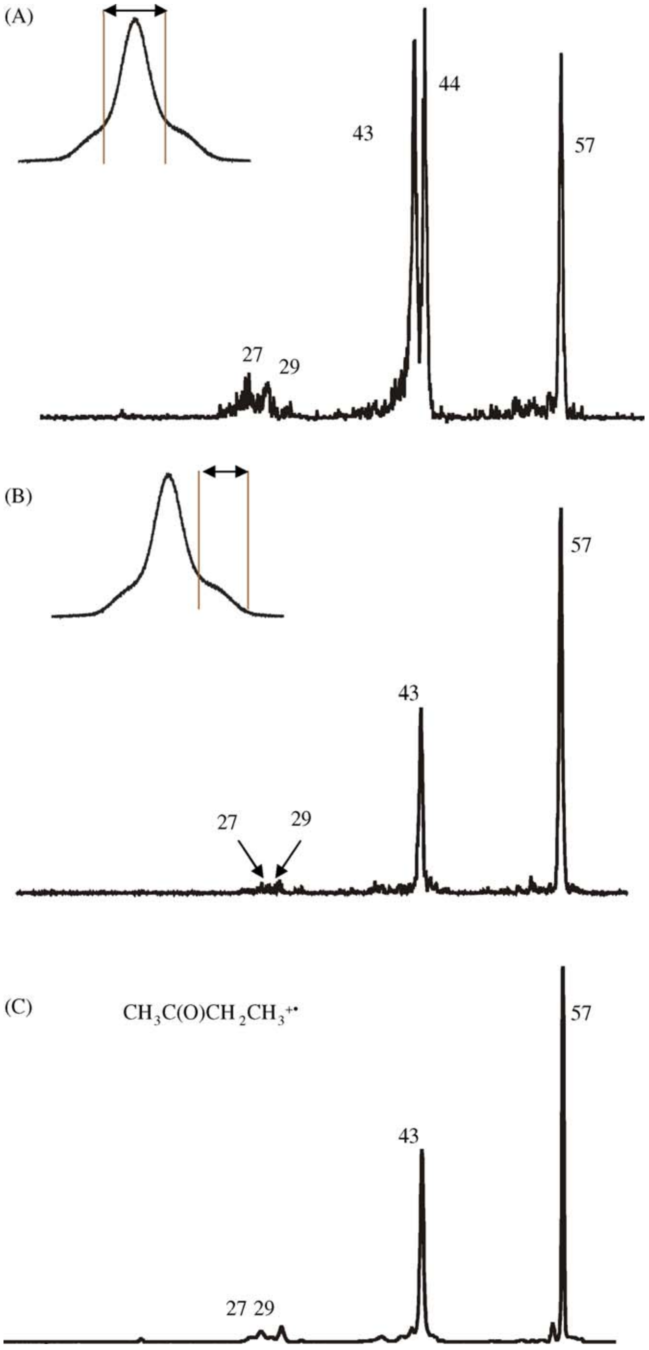


Fig. 2. CID mass spectra of: (A) the middle, (B) the edge component of the composite (M-28)$^{•+}$ peak and (C) ionized 2-butanone.

This is similar to that described by Meurer et al. [24], who regarded it as a loosely electron-bonded acylium ion dimer: $R_1–C{=}O^+\cdots e^-\cdots {}^+O{=}C–R_2$. In their paper, they observed *m*/*z* 43 ion as the base peak in the 70 eV EI mass spectrum of 2,3-pentanedione ion, contrary to their expectation based on the ionization energies of the two keto-radicals (IE ($CH_3CO^•$) = 7.0 eV [25] and IE ($CH_3CH_2CO^•$) = 6.75 eV [15], not 5.7 eV as quoted in [24]). However, when all the fragment ions arising from further dissociation of the *m*/*z* 57 and 43 ions are summed, the apparent discrepancy disappears.

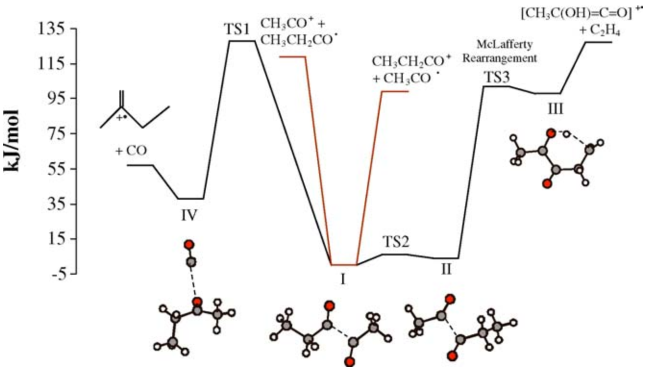


Fig. 3. Potential energy surface of the 2,3-pentanedione radical cation.

The calculated dissociation limits are 99 and 119 kJ/mol, respectively, corresponding to the two simple bond fragmentations in the 2,3-pentanedione ion. The PES also shows that the energy barriers for the two competing 28 amu loss channels are very close, i.e., 128 and 127 kJ/mol resulting from the loss of CO and C_2H_4, respectively. For the CO loss, the 2,3-pentanedione ion, I, rearranges to the stable state IV (38 kJ/mol) via TS1 (128 kJ/mol), an energy at which the three other dissociation processes can all kinetically compete within the MI time-frame. Stable state IV is represented as a 2-butanone ion electrostatically bound to CO by a long bond (3.404 Å), as shown in Fig. 4. The reverse activation energy barrier for this CO loss reaction is ca. 90 kJ/mol (128 − 38 kJ/mol) and this is in keeping with the significant KER peak observed in the MI mass spectrum (Fig. 1). In contrast, the loss of C_2H_4 does not involve a reverse energy barrier. TS3 is a 6-membered cyclic transition state for the 1,5-H transfer, corresponding to the McLafferty rearrangement and it lies at ca. 102 kJ/mol on the PES, which is ca. 25 kJ/mol below the dissociation threshold (127 kJ/mol) for the C_2H_4 loss. Structure III, having an enol structure, is the intermediate for this McLafferty rearrangement process and it loses ethene by cleavage of the α–β bond to produce a new ion, $CH_3C^{•+}(OH)C{=}O$, 2-hydroxymethyl ketene. Stable structure II is an isomer of ground state I, in which the ethyl group rotates and approaches the acetyl carbonyl group ($CH_3C{=}O$), followed by the McLafferty rearrangement.

The PES also summarizes the dissociation and rearrangement energy barriers for all the processes in the MI mass spectrum of 2,3-pentanedione. The energy difference between the highest and the lowest barrier is 29 kJ/mol and so the internal energy of the metastable ions lies in a 29 kJ energy band above the lowest dissociation limit. This energy range is typical for MI processes, giving relative peak abundances of from 1–2 to 100%.

The calculated product energies at the B3LYP/6-31+G(d) and G3 level of theory are shown in Table 1. 298 K G3 results are further compared with experimental data in Table 2, which shows that the accuracy of G3 calculations for the products is quite good, with the differences falling in the range of ±4 kJ/mol. Note that there is no direct experimental value for $\Delta_f H^\circ$ of the 2-hydroxymethyl ketene ion, $CH_3C^{•+}(OH)CO$. This can however usefully be estimated using the empirical relationship between $\Delta_f H^\circ$ and ln(*n*) (*n*: the number of atoms in the

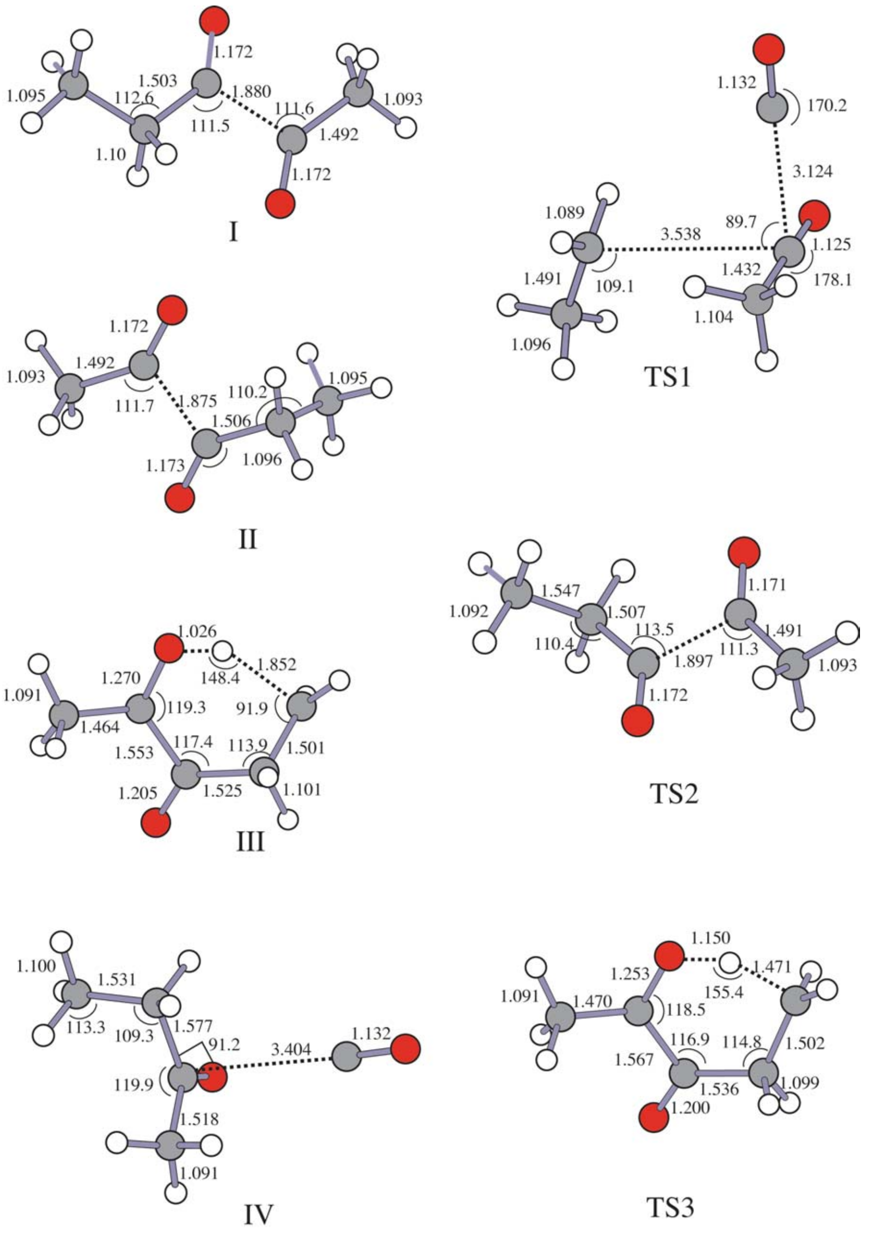


Fig. 4. Optimized geometries of the stable and transition states at B3-LYP/6-31+G(d).

ion) from the effect of –OH substitution in homologous ions [26]. $\Delta_f H^\circ[CH_3CH{=}C{=}O^{\bullet +}] = 783.5 \pm 0.3$ kJ/mol was determined by Traeger [27]; the substitution of –OH at C-2 lowered the enthalpy value by ca. 185 kJ/mol (obtained from the slope of the $\Delta_f H^\circ$ versus ln(n) plot), and thus $\Delta_f H^\circ[CH_3C^{\bullet +}(OH)C{=}O]$ was estimated to be 599 kJ/mol (784–185 kJ/mol). The calculated $\Delta_f H^\circ[CH_3C^{\bullet +}(OH)C{=}O]$ value 604 kJ/mol obtained from the G3 total energies (according to the atomization method reported by Nicolaides et al. [28]) is in good agreement with the estimated value.

Some additional comments deserve to be made concerning 2,3-pentanedione and its energetics. There is no experimental

Table 2
Comparison of the calculated product energies from the G3 level of theory (at 298 K) with experimental values

Products	G3 product energies (298 K)	Experimental product energies (298 K)	E_{rel} (G3 − experimental value)
$CH_3CH_2CO^+ + CH_3CO^\bullet$	606	609	−3
$CH_3CH_2CO^\bullet + CH_3CO^+$	625	627	−2
$CH_3CH_2C^{\bullet +}({=}O)CH_3 + CO$	570	566	4
$CH_3C^{\bullet +}(OH){=}C{=}O + C_2H_4$	656	652[a]	4

[a] Experimental data use the estimated $\Delta_f H^\circ[CH_3C^{\bullet +}(OH){=}C{=}O] = 599$ kJ/mol (see the text).

value for its $\Delta_f H^\circ$ but it can most readily be estimated by additivity or an equivalent method. For example, the known $\Delta_f H^\circ$ for 2,3-butanedione is −327.2 kJ/mol [29]; addition of the difference between $\Delta_f H^\circ[CH_3COCH_3] = -217.3 \pm 0.7$ kJ/mol [29] and $\Delta_f H^\circ[CH_3COCH_2CH_3] = -238.7 \pm 0.8$ kJ/mol [29], namely -21.4 ± 1.5 kJ/mol, gives an estimated $\Delta_f H^\circ[CH_3COCOCH_2CH_3] = -349 \pm 2$ kJ/mol, close to those reported by Kercher et al. [5], −348 and −344 kJ/mol. The ground state of ionized 2,3-pentanedione was found to have a very long OC–CO bond (see Fig. 4) and its $\Delta_f H^\circ$ was computed to be 513.7 kJ/mol at the G3 level. The adiabatic ionization energy (IE) is thus only 8.94 eV, slightly below the previously reported value of 9.1 eV [5] estimated from the molecule's photoelectron spectrum. From ref. [5], the vertical IE was ca. 9.4 eV, leading to an ion $\Delta_f H^\circ$ of 558 kJ/mol, an energy well on the way to the lowest dissociation limit at 609 kJ/mol (to produce $C_2H_5CO^+ + CH_3CO^\bullet$). Note that the McLafferty intermediate, ion III, lies in only a shallow potential well, unlike the analogous distonic ions from simple ketones ($\Delta_f H^\circ$ values for the latter can reliably be estimated using proton affinity (PA) data and alkyl C–H bond strengths, e.g., for $CH_3COCH_2CH_3{}^{\bullet+}$, $\Delta_f H^\circ = 677$ kJ/mol [25], and $\Delta_f H^\circ[CH_3C^+(OH)CH_2CH_2{}^\bullet] =$ ca. 667 kJ/mol, using $PA[CH_3COCH_2CH_3] = 827$ kJ/mol [30] and $D[RCH_2–H] = 420$ kJ/mol [15]). A computational exploration of alternative geometries for ion III did not disclose another minimum. The ion III is still less stable than its vertically ionized keto-analog, presumably as a result of a destabilizing influence by the (additional) CO group adjacent to the principal charge site (i.e., at $CH_3C^+(OH)$–); for example, the PA of $CH_3COCOCH_3$ is some 25 kJ/mol lower than that of $CH_3CH_2COCH_3$ [30].

3.2. *The dissociation characteristics of the 2,3-butanedione and 3,4-hexanedione radical cations*

We also investigated the dissociations of the homologous diketones, 2,3-butanedione and 3,4-hexanedione. The MI mass spectrum of ionized 2,3-butanedione (the biacetyl ion) is straightforward (Fig. 5), producing the acetyl ion (*m*/*z* 43, 100%) and a weak *m*/*z* 58 ion (ca. 1.9%) resulting from the loss of 28 amu. The CID mass spectrum of this *m*/*z* 58 ion is the same as that of the acetone radical cation and so *m*/*z* 58 arises from the loss of CO from the ionized 2,3-butanedione, a reaction analogous to that described for 2,3-pentanedione. The MI signal at *m*/*z* 58 is a flat-topped peak with a significant KER showing that this reaction similarly has a reverse energy barrier. The calculated dissociation threshold for this CO loss channel is 40.5 kJ/mol lower than that for the generation of the acetyl ion, using the following established experimental data: $\Delta_f H^\circ[CH_3COCH_3{}^{\bullet+}] = 719$ kJ/mol [25] and $\Delta_f H^\circ(CO) = -110.5$ kJ/mol [23], sum = 608.5 kJ/mol and $\Delta_f H^\circ[CH_3CO^+] = 659$ kJ/mol [13], $\Delta_f H^\circ[CH_3CO^\bullet] = -10$ kJ/mol [13,15], sum = 649 kJ/mol. The MI mass spectrum of 2,3-butanedione, with the acetyl ion as the base peak, indicates that the transition state for the CO loss reaction must lie above 649 kJ/mol, resulting in a significant KER. This result parallels the observations for the decarbonylation of ionized 2,3-pentanedione where the large KER component of the composite $(M-28)^{\bullet+}$ peak corresponded to CO loss with a remarkable energy difference between the transition state and the dissociation limit on the PES of 2,3-pentanedione.

Ionized 3,4-hexanedione is a symmetrical diketone and so the peak for the propanoyl ion (*m*/*z* 57 = 100%) dominates the MI mass spectrum (see Fig. 6). There are however some minor MI peaks: *m*/*z* 99 (ca. 10%), *m*/*z* 96 (ca. 1%), resulting from the loss of a methyl radical $(M-15)^{\bullet+}$ and the loss of H_2O $(M-18)^{\bullet+}$, respectively, and two very weak peaks at *m*/*z* 85 and 86 (both <1%). The *m*/*z* 86 peak (the loss of 28 amu) is composite, similar to the $(M-28)^{\bullet+}$ peak in the MI mass spectrum of ionized 2,3-pentanedione and thus can be expected to result from the loss of CO and C_2H_4. Because the large KER component of this composite peak is partially overlapped by the *m*/*z* 85 ion and because the signal was too weak, it was not transmitted to the next FFR in order to investigate each component's structure. When collision gas was added (to single collision conditions), *m*/*z* 85 $(M-29)^{\bullet+}$ increased three-fold, indicating that this ion arises from a simple bond cleavage, very likely the loss of an

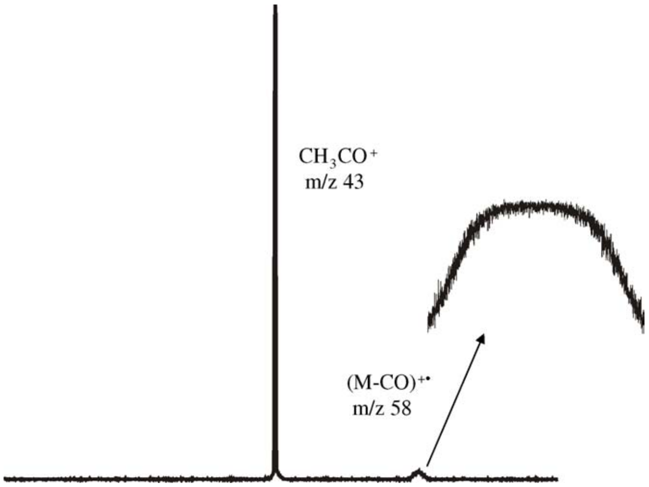


Fig. 5. MI mass spectrum of ionized 2,3-butanedione (*m*/*z* 86).

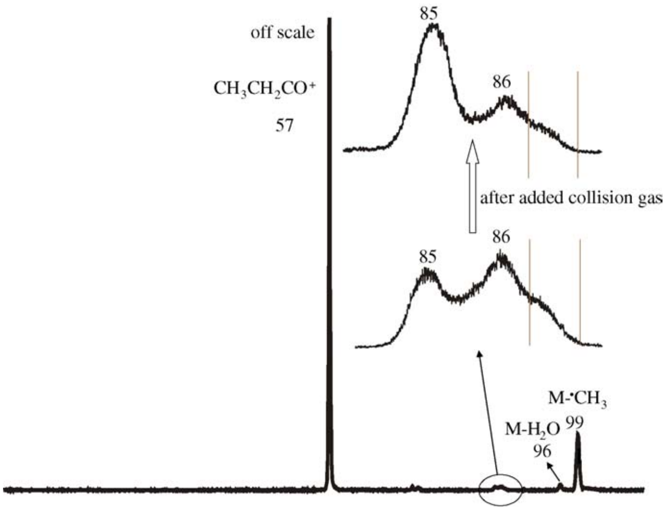


Fig. 6. MI mass spectrum of ionized 3,4-hexanedione (*m*/*z* = 114).

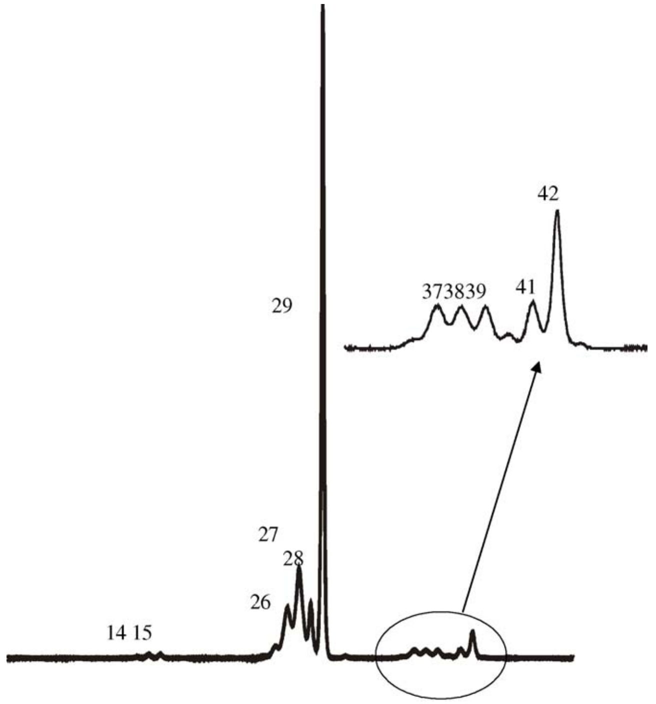


Fig. 7. CID mass spectrum of the *m*/*z* 57 ion generated from the metastable ionized diketones.

ethyl radical from the 3,4-hexanedione ion. We were asked (T. Baer, private communication) whether the *m*/*z* 57 product ion consisted of more than one component. The CID mass spectra of the *m*/*z* 57 ions from ionized 2,3-pentanedione, 3,4-hexanedione and 2-butanone generated in the ion source or as metastable ions are identical (Fig. 7). They do however contain very weak peaks at *m*/*z* 37, 38 and 39, indicating that a minor, high energy rearrangement can occur following collisional excitation. To check the hydrocarbon ion content of the *m*/*z* 42 ion in the above spectra, the *m*/*z* 42 fragment ion from a source-generated *m*/*z* 57 ion was transmitted into the 3FFR and its CID mass spectrum was recorded (see Fig. 8). This CID mass spectrum was identical with that of ionized ketene (which can directly be produced from ionized acetone) and shows no 37, 38 or 39 ions. We conclude that the hydrocarbon contamination in the *m*/*z* 57 ions is very minor indeed.

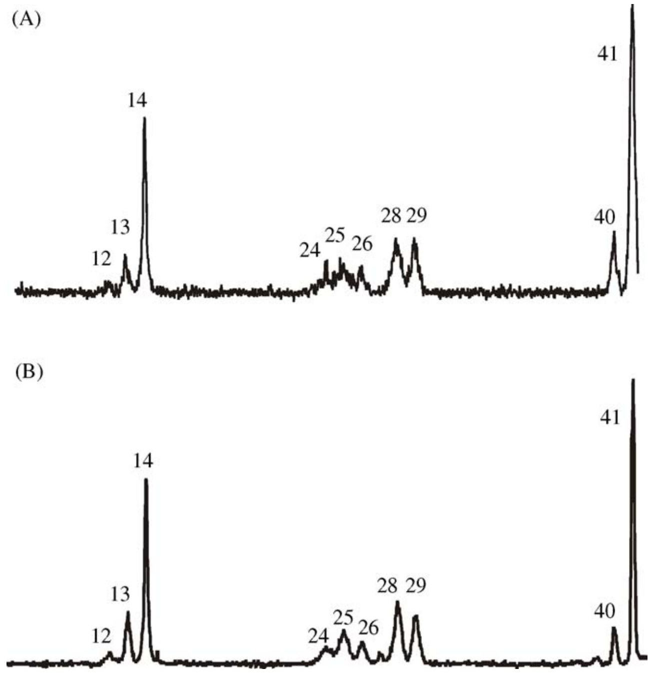


Fig. 8. CID mass spectra of: (A) the collision-generated *m*/*z* 42 ion produced from ionized 3,4-hexanedione and (B) ketene ion produced from ionized acetone.

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References

[1] A.J.C. Nicholson, Trans. Faraday Soc. 50 (1954) 1067.
[2] F.W. McLafferty, Anal. Chem. 28 (1956) 306.
[3] F.W. McLafferty, M.C. Hamming, Chem. Ind. (Lond.) (1958) 1366.
[4] F. Turecek, Encyclopedia of Mass Spectrometry, Elsevier, Amsterdam, 2005, p. 396.
[5] J.P. Kercher, E.A. Fogleman, H. Koizumi, B. Sztaray, T. Baer, J. Phys. Chem. A 109 (2005) 939.
[6] S. Coghe, H. D'Hollander, H. Verachtert, F.R. Delvaux, J. Inst. Brew. 111 (2005) 51.
[7] J.L. Holmes, J.K. Terlouw, Org. Mass Spectrom. 15 (1980) 383.
[8] R.G. Cooks, J.H. Beynon, R.M. Caprioli, G.R. Lester, Metastable Ions, Elsevier, Amsterdam, 1973.
[9] J.L. Holmes, P.M. Mayer, J. Phys. Chem. 99 (1995) 1366.
[10] E. Rennie, P.M. Mayer, J. Chem. Phys. 120 (2004) 10561.
[11] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, W.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 98 Rev. A. 7, Gaussian Inc., Pittsburgh, PA, 1998.
[12] A.P. Scott, L. Radom, J. Phys. Chem. 100 (1996) 16502.
[13] E.A. Fogleman, H. Kiozumi, J.P. Kercher, B. Sztaray, T. Baer, J. Phys. Chem. A 108 (2004) 5288.
[14] J.C. Traeger, R.G. McLoughlin, A.J.C. Nicholson, J. Am. Chem. Soc. 104 (1982) 5318.
[15] Y.-R. Luo, Handbook of Bond Dissociation Energies in Organic Compounds, CRC Press, Boca Raton, 2002.
[16] Z.A. Harvey, J.C. Traeger, J. Mass Spectrom. 39 (2004) 802.
[17] J.L. Holmes, in: P.B. Armentrout (Ed.), The Encyclopedia of Mass Spectrometry, Elsevier, Amsterdam, 2003, p. 91.
[18] P.C. Burgers, J.L. Holmes, C.E.C.A. Hop, R. Postma, P.J.A. Ruttink, J.K. Terlouw, J. Am. Chem. Soc. 109 (1987) 7315.
[19] D.H. Russell, M.l. Gross, N.M.M. Nibbering, J. Am. Chem. Soc. 100 (1977) 6133.
[20] L.N. Heydorn, P.C. Burgers, P.J.A. Ruttink, J.K. Terlouw, Int. J. Mass Spectrom. 228 (2003) 759.
[21] T. Drewello, N. Heinrich, W.P.M. Maas, N.M.M. Nibbering, T. Weiske, H. Schwarz, J. Am. Chem. Soc. 109 (1986) 4810.
[22] P.H. Goge, G.K. Hughes, J. Am. Chem. Soc. 72 (1950) 5570.

[23] J.D. Cox, D.D. Wagman, V.A. Medvedev, CODARA Key Values For Thermodynamics, Hemisphere Publishing Corp., New York, 1984.
[24] E.C. Meurer, F.C. Gozzo, R. Augusti, M.N. Eberlin, Eur. J. Mass Spectrom. 9 (2003) 295.
[25] S.G. Lias, J.E. Bartmess, J.G. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data 17 (Suppl. 1) (1988) 1.
[26] C. Aubry, J.L. Holmes, Int. J. Mass Spectrom. 200 (2000) 277.
[27] J.C. Traeger, Int. J. Mass Spectrom. 194 (2000) 261.
[28] A. Nicolaides, A. Rauk, M.N. Gluckhovtsev, L. Radom, J. Phys. Chem. 100 (1996) 17460.
[29] J.B. Pedley, R.D. Naylor, S.P. Kirby, Thermochemical Data of Organic Compounds, Chapman and Hall, London, 1986.
[30] E.P.L. Hunter, S.G. Lias, J. Phys. Chem. Ref. Data 27 (1998) 413.