The kinetic method as a structural diagnostic tool: ionized α-diketones as loosely one-electron bonded diacylium ion dimers

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The kinetic method is used to corroborate the description of ground state ionized α-diketones as loosely electron-bonded acylium ion dimers: $R^1-C=O^+---e^----{}^+O=C-R^2$. The abundance ratio of both the acylium ion fragments R^1CO^+ and R^2CO^+ (summed to those of their respective secondary fragments) formed upon low energy (5 eV) collision-induced dissociation of several ionized α-diketones is found to correlate linearly with the ionization energies (*IE*s) of the corresponding $R^1CO^•$ and $R^2CO^•$ free radicals as predicted by density functional theory calculations at the B3LYP/6-311++G(d,p) level. However, when these abundances are taken from 70 eV electron ionization mass spectra, lower and sometimes inverted ratios (2,3-pentanedione and 2,3-hexanedione) are observed. Inverted ratios are also observed via charge-exchange mass spectrometry/mass spectrometry (MS/MS) experiments for ionized 2,3-pentanodione formed with relatively high internal energies. Ionized α-diketones are found to display an effective temperature of 1705 K, which indicates an intermediate loosely-bonded nature. B3LYP/6-311++G(d,p) optimized geometries and charge and spin densities also corroborate the description of ground state ionized α-diketones as loosely electron-bonded diacylium ion dimers.

Introduction

The Cooks' kinetic method[1] is an attractive alternative for thermochemical measurements in the gas phase. To apply this mass spectrometric method, one should ideally employ gaseous *loosely-bonded* ionic asymmetric clusters (Equation 1), isolate them by mass-selection and then gently dissociated the ions to obtain the abundances of the two competing ionic fragments formed by breaking of the two weakest, loose bonds. From these abundances, ion affinities of the neutrals from the central ion are calculated. The method has been used extensively, and applied not only to measure ion affinities but also to access several other intrinsic chemical and thermodynamic properties of ions and neutral molecules. Its advantages include flexibility, ease of use and the ability to measure very small energy differences (~0.04 kJ mol^{-1}). Its applications are broad, covering proper-

ties such as proton and various ion affinities,[2] acidity,[3] electron affinity,[4] steric effects,[5] agostic bonds,[6] ionization energies,[7] entropy changes[8] and isotopic effects.[9] Perhaps the most outstanding feature of the kinetic method has been recently described: its ability to distinguish enantiomers and to precisely measure enantiomeric ratios.[10]

$$AX^+ + B \quad [A\text{---}X^+\text{---}B] \rightarrow A + BX^+ \qquad (1)$$
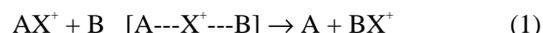
The kinetic method is based on a simple[1] linear relationship [Equation (2)]. In its simplest form, it assumes that if both the differences in the entropy changes for the competitive dissociation channels and the reverse activation energies are negligible (or similar), the intensity ratio I_{AX^+}/I_{BX^+} for the two adducts AX^+ and BX^+, formed when the gaseous and loosely-bonded ionic dimers [A---X$^+$---B] dissociate, correlates linearly with the affinity of the neutrals A and B to the central ion X$^+$ by Equation (2), in which R is the Boltzman constant, T_{eff} is the dimer effective temperature,[11] ΔH is the enthalpy difference of the two dissociation thresholds, and $\Delta(\Delta H)$ is the relative difference in affinity (or in bond dissociation energy) for the central ion.

This paper is dedicated to Professor Robert Flammang for his outstanding contributions to gas-phase ion chemistry

$$\ln\left(\frac{I_{AX^+}}{I_{BX^+}}\right) = \frac{\Delta(\Delta H)}{RT_{\text{eff}}} \qquad (2)$$

The method was initially designed to measure ion affinities,[1a] but soon it was realized that it could be used to access several other properties if properly-designed, *loosely-bonded* dimers are employed. For instance, intramolecular steric[5] and agostic[6] effects of several substituents (R) have been separated from electronic effects and measured by forming and dissociating, in the same reaction cells and via triple-stage (MS³) mass spectrometric experiments, both H⁺ and X⁺ (X = Cl⁺, Br⁺, SF₃⁺, PCl₂⁺, SiF⁺ or SiF₃⁺) cluster ions (**a**, Scheme 1). Similarly, both primary and secondary kinetic isotopic effects of substituents and the central ion have been measured by forming, selecting and dissociating ³⁵Cl⁺ and ³⁷Cl⁺ pyridine cluster ions (**b**).[5a] In an attempt to measure CH₃⁺ affinities, mixed alkyl nitriles dimers were formed and dissociated, and the kinetic method applied.[12] The method served as a structural diagnostic tool since the fragment ratios excluded loosely-bonded dimers, indicating otherwise a mixture of interconverting covalently-bonded structures (**c**). Enantiomeric composition has been measured using the method by forming, isolating and dissociating gaseous trimeric Copper(II)-bonded complexes of a chiral sample (A) with two molecules of a reference chiral compound (ref*, L-amino acids): [Cu^II(ref*−H)₂A−H]⁺.[10]

Ionization energies of organic compounds have also been determined using the kinetic method by dissociating radical cations of van der Waals complexes. Burinsky and co-workers[13] were the first to apply the kinetic method to determine electron affinities from mixed negative-ion dimers. Later, Cooks and co-workers formed ionized dimeric complexes of benzene and substituted benzenes,[14] generated by charge exchange CS₂ chemical ionization, and after mass-selection and dissociation by low-energy collisions with argon, the two individual radical cations were formed as the
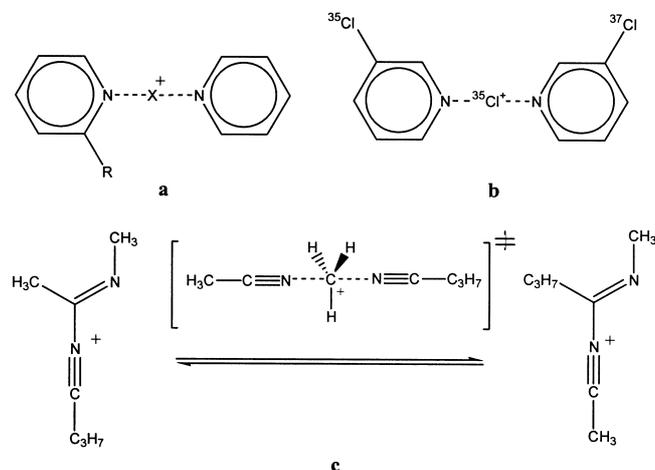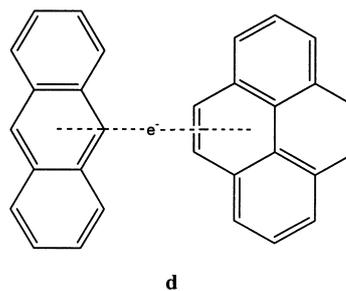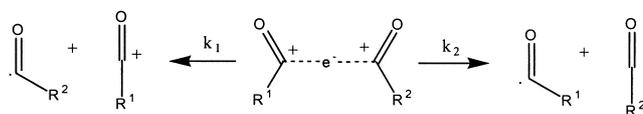

Scheme 2.

sole ionic fragments. The logarithm of the ratio of their abundances was found to correlate linearly with their ionization energies according to Equation 3.

$$\ln\left(\frac{I_{A^{+\cdot}}}{I_{B^{+\cdot}}}\right) = \frac{\Delta(IE)}{RT_{\text{eff}}} \qquad (3)$$

Recently,[4e] the kinetic method has been used to estimate electron affinities of PAHs by forming loosely one-electron bonded PAH heterodimers (Scheme 2, **d**). These heterodimers dissociate to give the two individual radical anions, and their abundance ratios were found to correlate linearly with ionization energies (*IE*s).

Although not yet extensively explored, an interesting alternative for expanding the benefits of the kinetic method is to apply it for ion structural characterization when the thermochemistries of the constituents are known or easily estimated. Cooks and colleagues[15] used the kinetic method to estimate *IE*s for benzyl radicals by measuring the relative abundances of the two benzyl cations in the electron ionization (EI) mass spectrum of substituted 1,2-diphenylethanes, and by assuming an unusual loosely one-electron bonded dicationic heterodimer structure for the ionized molecules. Their data demonstrated the applicability of the method to measure the free radical *IE*s, and have therefore additionally corroborated the proposed loosely-bonded structure of the parent ions.

α-Diketones, R¹C(=O)C(=O)R², dissociate promptly upon electron ionization by direct C–C bond cleavage to generate, to great extents, the respective R¹CO⁺ and R²CO⁺ acylium ions. This so extensive dissociation seems to indicate a loosely-bonded structure for the molecular ions, with major formation of the two acylium ions indicating an interesting electron bonded diacylium ion dimer structure for ionized α-diketones (Scheme 3). Note that such a character

Scheme 1.

Scheme 3

for the ground state ions is likely to be most pronounced for the transition state for unimolecular dissociation. The motivation of the present study was therefore to apply the kinetic method to corroborate the electron-bonded diacylium ion dimer structure proposed for ionized α-diketones. If so, the relative rates of competitive dissociation should correlate linearly by Equation (4) with the *IE*s of both $R^1CO^\bullet$ and $R^2CO^\bullet$ free radicals.

$$\ln\left(\frac{R^1CO^+}{R^2CO^+}\right) = \frac{\Delta(IE)}{RT_{eff}} \qquad (4)$$

Methods

Double-stage (MS[2]) mass spectrometric experiments[16] were performed with a Extrel (Pittsburgh, PA, USA) pentaquadrupole ($Q_1q_2Q_3q_4Q_5$) mass spectrometer.[17] The gaseous molecular ions of the α-diketones generated in the ion source were mass selected, and then dissociated by low energy (5 eV) collisions with argon thus producing the two competing acylium ions. The α-diketones formed in the ion source were mass selected by Q_1 and further dissociated by 5 eV collision dissociation in Q_4 with argon, while scanning Q_5 to acquire the spectra and operating Q_2 in the broad band rf-only mode. The 5 eV collision energy was taken as the voltage difference between the ion source and the collision quadrupoles. The indicated pressures in each differentially pumped region were typically 2×10^{-6} (ion source) and 8×10^{-5} (q_4) Torr, respectively. The 5 eV collision-induced dissociation (CID) product ion mass spectra were compared with 70 eV EI mass spectra taken from the NIST library.

Charge exchange MS/MS experiments were performed using the molecular ions of benzene, carbon disulfide, ethylene, oxygen, carbon dioxide or nitrogen, each formed in the ion source by 70 eV EI. The reactant ions were then mass-selected by Q_1 and subjected to charge exchange reactions in q_2 with the neutral α-diketone. Ion translational energies were set to near 1 eV as calibrated by the *m/z* 39 : 41 ratio in neutral ethylene/ionized ethylene reactions.[18] To record product ion mass spectra, Q_5 was scanned while operating Q_3 in the broadband rf-only mode.

Density functional theory (DFT) calculations were performed at either the B3LYP/6-311G++(d,p) or B3LYP/6-311G++(2df,2p) level of theory,[19] and molecular orbitals calculations performed by the AM1 semi-empirical method, were run on Gaussian 98.[20] Rice–Ramsperger–Kassel–Marcus (RRKM) calculations were performed using the MassKinetics program described elsewhere,[21] whereas vibrational frequencies were calculated using Gaussian 98.

Results and discussion

70 eV EI mass spectra

As a typical example, Figure 1 shows the 70 eV EI mass spectrum of 2,3-pentanodione as provided by the NIST
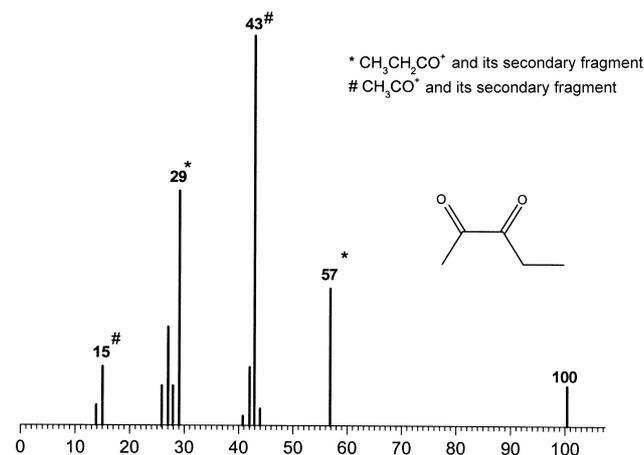

Figure 1. 70 eV EI mass spectrum of 2,3-pentanedione as provided by the NIST library.

library of mass spectra. The two acylium ions formed by cleavage of the C–C bond are those of *m/z* 57 ($C_2H_5CO^+$) and *m/z* 43 (CH_3CO^+). The *m/z* 57 : *m/z* 43 abundance ratio of these two acylium ions in the EI spectrum is near to 1 : 3. Under 70 eV EI, however, CO loss occurs to great extents for both primary acylium ions; hence the abundances of these secondary fragments, $C_2H_5^+$ of *m/z* 29 and CH_3^+ of *m/z* 15, should be summed to those of their respective parents, so a ratio of about 1 : 1.3 is re-calculated. Both ratios fail, however, to match that expected when considering a loosely one-electron bonded diacylium ion dimer configuration for ionized 2,3-pentanedione, and the expected *IE*s of competitive fragments. This is so because CH_3CO^+ of *m/z* 43, the base peak, corresponds to the free radical which displays the highest *IE*: $CH_3CO^\bullet$ (7.0 eV) and $C_2H_5CO^\bullet$ (5.7 eV);[22] hence upon dissociation of $CH_3C=O^+---e^----+O=CC_2H_5$, CH_3CO^+ should preferentially hold the electron, not the charge.[23] Note, however, that the accuracy of such a comparison during extensive dissociation upon 70 eV EI is limited since it depends heavily on our (in)ability to trace *all* fragment ions back to their respective acylium ions.

Similar measurements of the relative abundances of the two acylium ion fragments R^1CO^+ and R^2CO^+ (summed to those of the respective CO loss fragments), were performed from the 70 eV EI mass spectra of a series of α-diketones, and the results are collected in Table 1. To predict which acylium ion should dominate from the dissociation of a loosely-bonded one-electron dimer, the *IE*s of their respective acylium radicals were calculated using Gaussian 98 at the BLYP(6-311G(d,p) level (Table 2). Note that inverted abundance ratios of the two acylium ions are observed in the 70 eV EI mass spectra of both 2,3-pentanodione and 2,3-hexanedione, whereas the other α-diketones tested show the expected major acylium ion fragment under 70 eV EI (Table 1).

MS/MS experiments

To investigate whether the inverted ratios of 2,3-pentanodione and 2,3-hexanedione observed under 70 eV EI

Table 1. Abundance ratios for the two acylium ions (summed to that of their respective CO loss fragments[a]) as measured either for their 70 eV EI mass spectrum or 5 eV CID product ion mass spectrum, or predicted by B3LYP/6-311++G(d,p) calculations assuming a loosely electron-bonded diacylium ion dimer structure for the ionized α-diketones.

α-Diketone	R^1CO^+/R^2CO^+ abundance ratio				
	R^1CO^+	R^2CO^+	EI 70 eV	MS/MS (5 eV CID)	Predicted
4-Chloro-dibenzyl	Cl–C₆H₄–C⁺=O	C₆H₅–C⁺=O	0.3645	0.2221	< 1.0
m-Nitro-1-phenyl-1,2-propanedione	O₂N–C₆H₄–C⁺=O	CH_3-C⁺=O	2.3072	12.5867	> 1.0
2,3-Pentanedione	C_2H_5–C⁺=O	CH_3–C⁺=O	0.8196	13.0745	> 1.0
2,3-Hexanedione	C_3H_7–C⁺=O	CH_3–C⁺=O	0.2523	34.9501	> 1.0
Methyl-pyuvate	CH_3O–C⁺=O	CH_3–C⁺=O	0.0478	< 0.005	< 1.0
Butanoic-2-oxo acid	HO–C⁺=O	C_2H_5–C⁺=O	0.1523	< 0.005	< 1.0
1-Phenyl-1,2-propanedione	C₆H₅–C⁺=O	CH_3–C⁺=O	3.9627	> 200	> 1.0
Pyruvic aldehyde	CH_3–C⁺=O	H–C⁺=O	6.2217	> 200	> 1.0

[a]The intensities of secondary ions formed by CO loss from acylium ions were summed into those of the primary ions, that is, for CH_3CO^+ (CH_3^+), for $C_2H_5CO^+$ ($C_2H_5^+$), for $C_3H_7CO^+$ ($C_3H_7^+$), for $PhCO^+$ (Ph^+), for (Cl–$C_6H_4CO^+$), Cl–$C_6H_4^+$), and for NO_2–$C_6H_4CO^+$ (NO_2 $C_6H_4^+$)

conditions are an effect of excess internal energy of the unstable dissociating ions, (meta)stable ionized α-diketones leaving the EI ion source (hence ions expected to display very low contents of internal energy since a low energy threshold is expected for their unimolecular dissociation) were mass selected and then dissociated in MS/MS experiments under mild 5 eV energy collisions with argon. Figure 2 shows, as a representative example, the 5 eV CID product ion mass spectrum of ionized 2,3-pentanedione. Now, under the mild 5 eV collision conditions, primary C–C bond cleavage dominates, the ion of m/z 57 becomes by far the major fragment, and the m/z 57 : m/z 43 ratio is much greater than 1. Ionized 2,3-hexanedione also fragments under 5 eV CID in a similar way yielding a $C_3H_7CO^+$: CH_3CO^+ ratio much greater than 1 (Table 1). For the other α-diketones, the gentle 5 eV CID conditions enhances considerably the relative abundances of the acylium ion fragment with the lower IE, as compared with the ratios observed in the 70 eV EI mass spectrum. Under 5 eV CID conditions, therefore, the dissociation behavior of *all* ionized α-diketones investigated corroborates the proposed loosely electron-bonded diacylium ion dimer structure $[R^1CO^+---e^-----^+OCR^2]$, and reflects closely the IEs preferences of the acylium fragments to hold the electron or the charge.
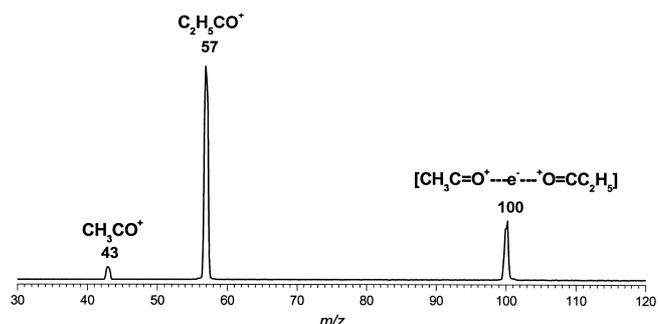

Figure 2. CID (5 eV) product ion mass spectrum of ionized 2,3-pentanedione.

Table 2. Ionization energies of free radicals as predicted by B3LYP/6-311++G(d,p) calculations.

Free radical	RCO$^\bullet$ energy (hartrees)	RCO$^+$ energy (hartrees)	*IE* (eV)
CH_3—•=O	−153.2319675	−152.969678	7.14
C_2H_5—•=O	−192.5562734	−192.3028828	6.89
C_3H_7—•=O	−231.8807628	−231.6321273	6.77
(phenyl)—•=O	−345.0062956	−344.7784065	6.20
Cl—(phenyl)—•=O	−804.6382988	−804.3976002	6.55
CH_3O—•=O	−228.4715915	−228.1963744	7.49
HO—•=O	−189.1588881	−188.8566339	8.23
CH_3CH_2O—•=O	−267.8022386	−267.5424582	7.07
O_2N—(phenyl)—•=O	−549.5679985	−549.3168292	6.84

For the above examples, the kinetic method can be used to corroborate further the existence of the proposed $[R^1CO^+$---e^----$^+OCR^2]$ structure. This can be assessed by testing whether a linear relationship [using Equation (4)] exists between the acylium ion abundance ratios as measured by 5 eV CID and the difference in ionization energies (ΔIEs) of their respective free radicals. A plot of $\ln(R^1CO^+/R^2CO^+)$ from the 5 eV CID spectra of 2,3-pentanedione, 2,3-hexanedione, *p*-chloro-benzile and *m*-nitro-1-phenyl-1,2-pentanedione (only α-diketones which display measurable abundances of the two acylium ion fragments can be used) versus the calculated ΔIEs (Table 2) was therefore constructed (Figure 3). The relatively high correlation coefficient (0.994) of such a plot provides therefore additional evidence for the loosely-bonded proposed structure. From the angular coefficient [Equation (4), $1/RT_{eff}$], an effective temperature (T_{eff}) for the dimer of 1705 K is measured. Such a T_{eff} indicates an intermediate loosely-bonded nature[1] since more typical T_{eff} for weakly bonded species are below 1000 K whereas covalently bonded species display considerably higher (greater than 2000 K) effective temperatures.[24]

Charge-exchange MS/MS experiments

To investigate further the effect of excess internal energy, charge-exchange MS/MS experiments with mass-selected reagent gases of increasing ionization energies were performed for 2,3-pentanedione. The main idea was to generate the ionized molecule with increasing, predictable internal energies above the threshold for unimolecular dissociation. Ions with known and increasing *IE*s were therefore formed in the ion source, mass selected by Q1, and then reacted with neutral 2,3-pentanedione in the first collision cell (q2) of the pentaquadrupole mass spectrometer. Charge exchange occurs and the "hot" ionized α-diketone molecules dissociate in turn to both CH_3CO^+ and $C_2H_5CO^+$ (and eventually but to limited extents by further CO loss) due to the energy liberated in the exothermic charge-exchange reaction. The absolute abundances of the competitive fragments were then plotted as a function of the internal energy expected to be deposited into the ionized 2,3-pentanodione molecule (Figure 4).

Knowing that the *IE* of 2,3-pentanedione is near 9.75 eV[25] and using ionized molecules with *IE* from 9 to 16 eV, a comprehensive profile of the dissociation behavior
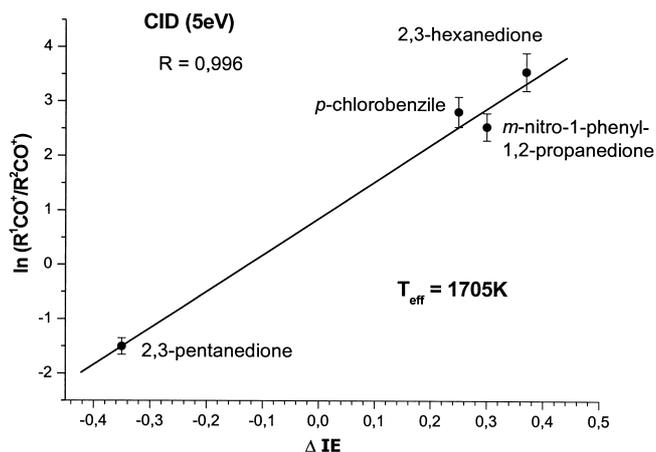
Figure 3. Plot of $\ln(R^1CO^+/R^2CO^+)$ versus calculated ΔIEs (see Table 2) for α-diketones which display the two acylium ion fragments with measurable abundances in their 5 eV CID product ion mass spectrum.

Figure 4. Plot of the abundances of the CH_3CO^+ ($+ CH_3^+$) and $C_2H_5CO^+$ ($+ C_2H_5^+$) fragment ions versus the IEs of the reactant ion in mass-selected charged-exchange reactions with 2,3-pentanedione.

of ionized 2,3-pentanedione as a function of its internal energy could therefore be obtained. Charge exchange with ionized benzene, carbon disulfide and ethylene, those molecules with IEs closer to that of 2,3-pentanodione, generate ionized 2,3-pentanodione which dissociates as expected for $CH_3C=O^+ \text{---} e^- \text{---} {}^+O=CC_2H_5$, that is, the lighter acylium ion with the higher IE holds preferentially the electron and consequently $C_2H_5CO^+$ of m/z 57 is the main ionic fragment. But the relative intensity of the competitive CH_3CO^+ fragment ion increases steadily with internal energy. Charge exchange with $O_2^{+\bullet}$ should yield molecules of ionized 2,3-pentanodione with near 2.3 eV internal energy, and these relatively hot ions dissociate to form $C_2H_5CO^+$ ($+C_2H_5^+$) and CH_3CO^+ ($+CH_3^+$) with near the same abundances. The inversion observed under 70 eV EI-induced dissociation than occurs for charge exchange with $CO_2^{+\bullet}$ and $N_2^{+\bullet}$, for which the most exothermic charge-exchange reactions occur yielding substantially hot 2-3pentanedione molecular ions.

Note that this inversion so clearly seen here for the unimolecular dissociation of ionized 2,3-pentanedione by the internal-energy controlled charge-exchange MS/MS experiments, is a well-known phenomenon, actually a long-standing mystery in gas-phase ion chemistry,[26] and this example adds several others in which smaller fragment are preferentially lost from radical cations at low energies and larger ones at high energies. McAdoo and co-workers have recently studied this phenomenon, both experimentally and theoretically, and provided an explanation: near threshold, losses of smaller radicals are favored relative to losses of larger ones because the losses of smaller radicals are energetically favored (as is the case here for ionized 2,3-pentanedione dissociation). Losses of larger radicals become dominant, however, with increasing energy because these losses proceed through looser transition states.[26] This explanation is also supported by formation of long CC bonds
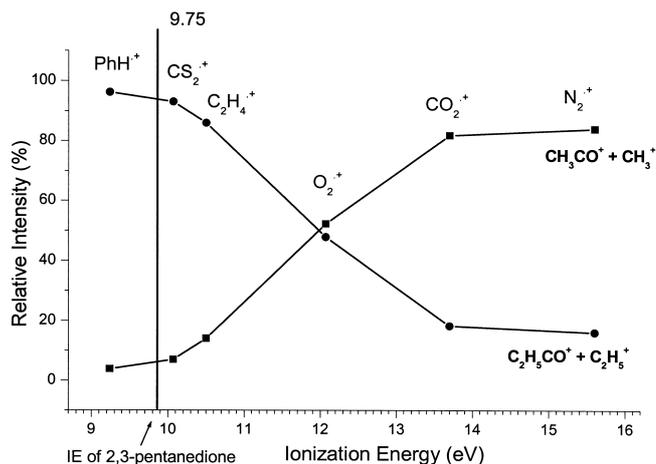
to alkyl groups in the parent ion even in its ground state. Note also that differences in energy thresholds for consecutive dissociations leading to different depletion rates for the two competitive fragment ions (usually lower thresholds hence faster rates are seen for larger ions) cannot be used here to explain the observed inversion in abundance ratios because secondary fragments were traced back to the acylium ions.

RRKM calculations

The RRKM theory is capable of accurately and quantitatively describe both microcanonical and canonical rate constants without the need of empirical parameters.[27] The total internal energy-dependent microcanonical rate expression is given by Equation (5), where E_0 is the critical energy, $W^{\#}(E^* - E_0)$ is the sum of the states in transition state with internal energy of $E^* - E_0$, $N(E^*)$ is the density of states at E^* internal energy, σ is the reaction path degeneracy and h is Plank's constant.

$$k(E^*) = W^* \cdot \sigma \frac{(E^* - E_0)}{hN(E^*)} \quad (5)$$

To test the relationship between the internal energy of ionized 2,3-pentanone and the branching ratio for the rates of the competitive formation of acetyl and propionyl cations, calculations were performed using the RRKM theory. A "loose" transition state model was used.[28] The difference in the critical energies for both channels, E_{01} and E_{02}, can be taken as the difference in the ionization energy (ΔIE, Table 2) of the two radicals, given that the activation energies for the reverse reactions are insignificant. This is reasonable for simple bond cleavage of loosely bounded dimers, as illustrated by previous examples.[29] The energy required to form the ion of m/z 43 from ionized 2,3-butanedione (appearance
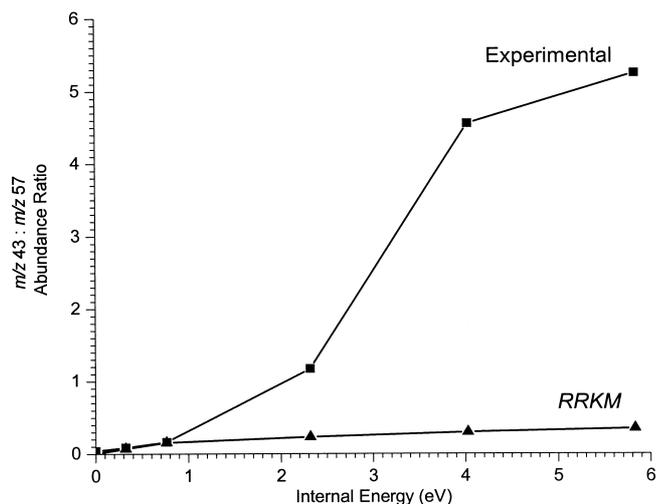
Figure 5. Plot of the CH$_3$CO$^+$ (*m/z* 43) : C$_2$H$_5$CO$^+$ (*m/z* 57) fragment ion abundance ratios as a function of internal energy for the dissociation of ionized 2,3-pentanedione as measured experimentally or predicted by RRKM theory.

Figure 6. Main structural parameters of ionized and neutral 2,3-pentanedione from structural optimization at the B3LYP/6-311++(2df,2p) level.

Scheme 4.

energy) was found to be 0.31 eV.[30] This is a good approximation for the critical energy (E_{02}) to form the acetyl cation from ionized 2,3-pentanedione. Therefore, the critical energy to form the propionyl cation is $E_{01} = 0.06$ eV: $\Delta IE - E_{02}$.

Figure 5 shows the plot of the fragment ion abundance ratios (*m/z* 43 : *m/z* 57) as a function of the internal energy of the ionized 2,3-pentanedione calculated by RRKM theory. The predicted fragment abundance ratios, representing the ratios of rate constants (k_1/k_2) for both channels, increases with increasing internal energy and tends to reach unity. This is consistent with previous studies on similar proton-bound dimers.[31] But when compared with the experimental ratio, the discrepancy is evident as the experimental ratio exceeds 1 (inversion) and reaches values higher than 5 for the highest internal energy.

Structural calculations on ionized α-diketones

Figure 6 compares the optimized structure of 2,3-pentanedione both in its neutral and ionized forms. The optimized ground state structure of ionized 2,3-pentenedione display much of the properties expected for the proposed loosely electron-bonded diacylium ion dimer: the C---C bond distance is as long as 1.96 Å, too long for a covalently bonded structure and much longer than that in the neutral form (1.54 Å), the R–CO bond angles of 124° for the carbonyl groups in the neutral form enlarges to 138° in the ionized form, and the C=O bond in the ionized form contracts from 1.21 Å to 1.16 Å.

B3LYP/6-311++G(2df,2p) calculations for ionized 2,3-hexanedione and benzile were also performed, and structures with features similar to that calculated for ionized 2,3-pentanedione were obtained (Scheme 4). These predictions further corroborate the description of ground
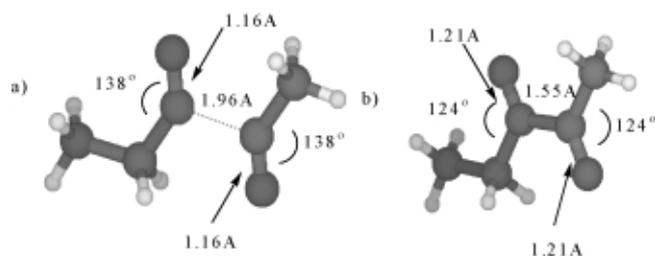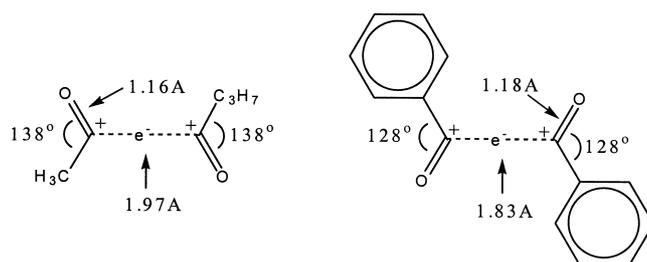
state ionized α-diketones as loosely electron-bonded diacylium ion dimer. This loosely-bonded character is likely to be further enhanced, actually to be at a maximum in the transition state of the unimolecular dissociation. There are a number of examples in the literature where the initially generated molecular ions of conventional structures spontaneously rearrange to a more stable species characterized by a long one-electron C–C bond, which include the molecular ions of CH$_3$OC(=O)C(=O)OCH$_3$, HOCH$_2$CH$_2$OH, HOCH(CH$_3$)CH$_2$OH and CH$_3$C(=O)–CH$_2$OH.[32]

SOMO

Molecular orbitals calculations with the AM1 semi-empirical method[33] were also performed to investigate the electron-bonded cationic heterodimer nature of ionized α-diketones. As seen in Figure 7, the singly-occupied molecular orbital (SOMO) of ionized 2,3-pentanedione is that formed by the combination of the σ$_{c-c}$ orbital and the p$_x$ oxygen atomic orbitals. The unpaired electron density is therefore high between the two carbonyl C atoms, and this description also corroborates the proposed loosely electron-bonded diacylium ion dimer structure.

Charge and spin density

The B3LYP/6-311++G(2df,2p) spin density and Mulliken charge distributions (in parenthesis) of ionized 2,3-pentanedione also corroborates a loosely electron-bonded diacylium ion dimer structure (Figure 7). Spin density (the unpaired electron) is high on the two carbonyl oxygens and also between the two carbonyl carbons, as
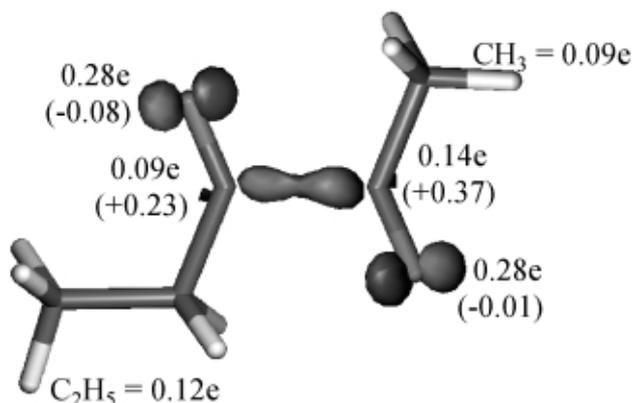
Figure 7. SOMO orbital of ionized 2,3-pentanedione, and the spin densities and total atomic charges (in parenthesis) of ionized 2,3-pentanedione, with hydrogens charges added to heavy atoms.

expected for an one-electron bonded diacylium ion dimer. The positive charge is mainly located on both the two carbonyl carbons, again as expected for an acylium ion dimer.

Final remarks

Theoretically, the description of ground state ionized α-diketones as the unusual and interesting loosely electron-bonded[34] diacylium ion dimers $[R^1–C=O^+ \!-\!\!-e^-\!\!-\!\!^+O=C–R^2]$ has been supported by B3LYP/6-311++G(2df,2p) optimized geometries and charge and spin densities. Experimentally, evidence for such structures is provided by the kinetic method from the intermediate effective temperature of the dimer (T_{eff} = 1705 k), and the linear correlation between the abundance ratio of both the acylium ion fragments R^1CO^+ and R^2CO^+ (summed to that of their respective CO loss fragments) formed upon low energy 5 eV collision-induced dissociation of ionized α-diketones with the *IE*s of their corresponding $R^1CO^•$ and $R^2CO^•$ free radicals, as predicted by DFT calculations at the B3LYP/6-311++G(d,p) level. Abundance ratios of acylium ion fragments taken from 70 eV electron ionization mass spectra are often much lower (than those expected from relative *IE*s) and sometimes even inverted, as an effect of excess internal energy of the parent ion which tend to favor the smaller acylium ion (by favoring the loss of the larger radical). Herein, this ratio invertion with increasing internal energy has been seen clearly for the molecular ions of 2,3-pentanedione and 2,3-hexanedione, particularly when internal energy controlled charge-exchange MS/MS experiments were performed for 2,3-pentanedione. Hence, when the thermochemistry of the species is known or can be easily estimated, the kinetic method becomes a suitable candidate for a tool to prove structures of gaseous ions.

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