International Journal of Mass Spectrometry 273 (2008) 117–125

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Partial ionization cross-sections of acetone and 2-butanone

J.R. Vacher*, F. Jorand, N. Blin-Simiand, S. Pasquiers

Laboratoire de Physique des Gaz et des Plasmas, UMR CNRS 8578, Bât. 210, Université Paris XI, 91405 Orsay Cedex, France

ARTICLE INFO

Article history:
Received 1 February 2008
Received in revised form 21 March 2008
Accepted 21 March 2008
Available online 30 March 2008

Keywords:
Ionization cross-section
Mass spectrometry
VOC decomposition
Acetone
2-Butanone

ABSTRACT

The electron impact ionization of acetone and 2-butanone between 10 and 86 eV has been studied using mass spectrometry. The cross-sections are measured for the formation of molecular ions and major fragment ions which are produced. The present results display good agreement between the measured total ionization cross-sections and the calculated with the BEB model. The enthalpies of formation and the ionization energies of several fragments are evaluated using ab initio calculations. For each ketone, the molecular ion and the 43 amu ion contribute to about 80% of the total cross-section at 86 eV. The 43 amu ion, identified as the acetyl cation, is the most abundant above 15 eV. Other ions present in the spectra of acetone are (i) the 42 amu ion, detected in the range 12–86 eV, contributes to about 6% of the total cross-section at the maximum voltage used and is identified at low energy as a ketene cation, (ii) six other minor ions (39, 27, 26, 44, 29 and 15 amu) were detected above 17 eV. Five of them may result from dissociation reactions of the molecular ion while the methyl cation is issued from the 43 amu ion. In the spectra of 2-butanone, other ions are (i) the 57 amu ion detected in the range 11–86 eV and identified as the propionyl cation, contributes to about 6% of the total cross-section over the whole ionization energy range, (ii) four other minor ions (42, 29, 27 and 15 amu) were detected above 18 eV and there formation is similar to that of acetone. Effects of fragment size favour from the molecular ion, the formation of the 57 amu ion near the threshold, and at higher energy, the formation of the 43 amu ion.

1. Introduction

Acetone and 2-butanone(methyl-ethyl-ketone) are widely used in industry. They are typical volatile organic compounds (VOCs) released in the atmosphere and contribute to the formation of pollutants, especially in urban areas. These two ketones represent about 5% of the anthropogenic VOCs emission [1] and their destruction, mainly by photolysis and reaction with the OH radical [2,3], has an impact in atmospheric chemistry. Their atmospheric reactions yield particularly harmful products, leading to tighter legislation. For example, the Göteborg protocol (1999) stipulates that the VOCs released in the atmosphere must be reduced by 35% before 2010.

A growing interest has developed in the removal of VOCs in air using pulsed discharges [4,5] but much work remains to be done in order to understand all the physical and chemical processes involved in the conversion of these pollutants into less harmful molecules. Kinetic models to describe the plasma reactivity in gas phase including $N_2/O_2/H_2O$ with the addition of one VOC are currently being developed. Validation of these models through the comparison of predictions with various measurements of radical and molecule densities (chromatography, LIF, FTIR spectroscopy, etc.) is an important step in the optimization of "de-VOC" processes by non-thermal plasmas. In these conditions, the role of VOC oxidation by O atoms and OH radicals is the most important reactional pathway for the destruction of the molecule, but at room temperature, electron collisions should have a non-negligible influence when the oxidation reaction rates are low. This later process can produce important reactive species such as methyl radicals, hydroxyl radicals and ions which can participate in the VOC removal through dissociative charge transfer reactions, or aggregation leading to the formation of polymers.

In the present paper, mass spectrometry measurements of the electron impact ionization of acetone and 2-butanone are reported, cross-sections for the formation of fragment ions are measured and partition processes leading to observed ions are suggested. These results are useful data for kinetic models involving ion-molecule reactions running in VOC conversion processes using photo-triggered discharges [6–8].

2. Experimental and theoretical method

2.1. Experimental

The experimental set-up described elsewhere [9–12], has been improved by modification, of the polarizations into the ionization chamber and the vacuum system. The measurements are made

---

* Corresponding author. Tel.: +33 169 157 497.
E-mail address: jean-rene.vacher@u-psud.fr (J.R. Vacher).

1387-3806/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2008.03.011

with xenon whose ionization threshold of 12.13 eV [13] is smaller than for argon (15.76 eV [13]) which was used previously [12]. This choice allows the measurement of the cross-sections in the range 13–16 eV in which it is possible to obtain more useful information on the nature of the ions. The VOC (acetone: Prolabo, 99.7%; 2-propanone: Acros organics, 99.5%) is introduced at room temperature, through a septum, into a stainless-steel reservoir at 10^{-3} Torr residual pressure. The vapour is introduced into a gas container at a partial pressure of less than 1 Torr so as to prevent condensation of the VOC compounds. The formation of condensation droplets has to be avoided at cold spots. The stability of the pressure is checked before the addition of xenon (Air Liquide, 99.95%) in the gas container. The pressures are measured with a precision of 0.001 Torr; the partial pressure of xenon is twice that of VOC. The gas mixture is first admitted into a gas-holder at a controlled pressure of 0.5 Torr, and then admitted, through a 50 μm diameter hole, into the analysis chamber. To reduce water impurities, the inlet gas set-up is previously baked so that the remaining pressure is as low as 10^{-8} Torr.

Ions are formed in the ionization chamber (at a constant pressure of 2×10^{-6} Torr) by the impact of a focused electron beam over the energy range 10–86 eV. Based on a comparison with rare gas ionization thresholds, the electron energy is estimated to be measured at ±0.5 eV. The ions are then accelerated, focused and mass analysed in a quadrupole mass spectrometer with a resolution ($M/\Delta M$) better than 400. The various ionic species are detected by means of a channel-electron multiplier followed by a Faraday cup and the collected current then recorded by a computer (which also controls all set-up functions). The ratios of the intensity of VOC ionic fragments to that of Xe^+ ions give the cross-sections for the formation of the fragments relative to that of xenon ionization, the partial pressures of acetone or 2-butanone and of xenon being known. Several authors have measured the ionization cross-section of xenon [14–18]. Among them, Wetzel et al. [14] give the more accurate values near the threshold and thus, these values are used in the further calculations.

It is well known that the transmission through the quadrupole strongly depends on the analysed masses. Thus, the transmission factor caused by mass segregation into the analyser is taken in account [10,11]. In order to estimate the precision of our results, we measured the ionization cross-section of argon with Ar substituted for VOC. We found fluctuations of ±10% compared to the values given by Wetzel et al. [14] between 20 and 86 eV and fluctuations of ±20% below 20 eV.

Discrimination effects may result from the extraction process of fragment ions out of the ion source and from the introduction of the ion beam into the mass analyser. This discrimination is due to the formation of fragment ions from a molecule with a kinetic energy of several electron volts and with a velocity component normal to the axis of the system. This discrimination reduces the number of ions of a given mass which can be detected [19] and thus reduces the cross-section for the formation of this ion. It is important to verify the complete collection of the energetic fragment ions in order to do conclusive measurements [20]. A detailed analysis of the experimental uncertainties in measurements of absolute partial cross-section using time-of-flight (TOF) mass spectrometer has been given by Straub et al. [21]. Using a position-sensitive detector, they observed the positional distribution of the energetic fragment ions and they demonstrated that all of the energetic fragment ions were collected with the TOF mass spectrometer. Jiao et al. [22] using Fourier-transform mass spectrometry (FTMS) have reported the cross-section for electron impact ionization of trifluoromethane and funded excellent agreement with previously reported results by time-of-flight experiments but larger than results issued from quadruple mass spectrometric detection. They remark that the FTMS sensitivity is independent of the ion mass and chemical composition and as no ion current is collected, no calibration factor associated with the collection efficiency is necessary.

Our experimental device does not allow to highlight the effect of the excess energy on the mass spectra. In order to test the validity of our measurements, we measured ionization cross-section of a heavy molecule. We used *n*-octane for which cross-sections for the formation of ions were measured by Jiao et al. [23]. We checked for masses 43, 41, 85, 57, 29, 71, 56 and 114 at 20, 50 and 70 eV. For these values, our results were consistent with those of Jiao et al. within 20%. These results seem to indicate that no severe discrimination occurs in our apparatus for these masses and these energies.

2.2. Theoretical

The geometrical optimizations and the total electronic energies for the studied molecules, radicals and ions of which data are not given in the literature, were performed with the 6-31G(d) basic set using the B3LYP theoretical method. This standard level basic set allows to optimise the determination of structures and to compare the enthalpies of formation of the species. The ionization energies were computed as being the difference between the enthalpies of the fully optimised neutral molecules and that of the corresponding radical cations. The use of larger basic sets does not modify significantly the relative energies. All the optimised geometries corresponding to a minimum point have real frequencies. Thermodynamic gas-phase data were computed at 298.15 K and 1 atm using the internal thermal energy and the absolute entropy of each species. Ab initio calculations were carried out using the Gaussian 03 series of programs [24]. Calculated heats of formation and ionization energies are given Table 1 with data given in the literature.

The cross-section for ejecting an electron from an orbital by electron impact can be calculated using the Binary–Encounter–Bethe (BEB) model developed by Kim et al. for atoms [25] and molecules [26]. This cross-section is given by

$$\sigma_{\mathrm{BEB}}(T) = \frac{S}{t+u+1}\left[\frac{Q\ln t}{2}\left(1-\frac{1}{t^2}\right)+(2-Q)\left(1-\frac{1}{t}-\frac{\ln t}{t+1}\right)\right]$$

where $S = 4\pi a_0^2 N(R/B)^2$ with $a_0 = 0.529$ Å, $R = 13.61$ eV, N is the electron occupation number, B is the orbital binding energy, $t = T/B$ with the incident electron kinetic energy T, $u = U/B$ with the orbital kinetic energy U and Q is an integral on the continuum dipole oscillator strength which to a good approximation is routinely set equal to 1 [27]. The total single ionization cross-section is given by the sum over all the occupied molecular orbitals:

$$\sigma(T) = \sum \sigma_{\mathrm{BEB}}(T)$$

The values of each orbital binding energy and orbital kinetic energy of the two ketones in the ground state were obtained using ab initio calculations at the medium RHF/6-31G(d) level of theory which gives reliable values of orbital binding energies. Twelve of these orbitals contribute to the BEB cross-section below 100 eV for acetone and fifteen for 2-butanone. To ensure that cross-sections start at the ionization threshold, the calculated binding energies of the highest occupied molecular orbitals (HOMOs) are replaced by the experimental values of the ionization energies. The results of theoretical determinations of electron impact ionization cross-sections depend on the ab initio level of theory used [28,29]. With no empirical corrections to the binding energies, the BEB method gives cross-sections slightly lower than those measured [30]. Empirically adjusted orbital energies can reconcile the difference between computed and measured cross-sections but such corrections were not taken into account in our study.

Table 1
Heat of formation of the neutral species and corresponding ionization energies (IE) from NIST [13], except (a) and (b)

Mass (amu)	Formula	N name	$\Delta_f H_{298\,K}^{\circ}$ (kJ mol^{-1})	S IE (eV)
1	H	Atomic hydrogen	218.0	13.60
13	CH	Methylidyne	594	10.64
14	CH_2	Methylene	386.39	10.40
15	CH_3	Methyl	145.7	9.84
16	O	Atomic oxygen	249.18	13.62
16	CH_4	Methane	−74.87	12.61
18	H_2O	Water	−241.83	12.62
26	C_2H_2	Acetylene	226.73	11.40
27	C_2H_3	Vinyl	299	8.25
28	C_2H_4	Ethene	52.47	10.51
28	CO	Carbon monoxide	−110.53	14.01
29	C_2H_5	Ethyl	119	8.13
29	HCO	Formyl	43.51	8.12
30	C_2H_6	Ethane	−84.7	11.52
31	CH_2OH	Hydroxymethyl	−9	7.56
31	CH_3O	Methoxyl	17	10.72
32	CH_3OH	Methanol	−201	10.84
39	c-C_3H_3	Cyclopropenyl	443	6.6
39	l-C_3H_3	Propargyl	339	8.67
42	CH_2CO	Ketene	−47	9.62
42	CH_3CHCH_2	Propene	20.41	9.73
43	CH_3CO	Acetyl	−12	7.0
43	C_2H_3O	Vinyl oxide	134[a]	7.3[b]
43	c-C_2H_3O	Oxiranyl	163[b]	7.5[b]
43	C_3H_7	Propyl	100	8.10
44	CH_3CHO	Acetaldehyde	−166.2	10.23
44	CH_2CHOH	Ethenol	−128	9.33
45	C_2H_5O	Ethoxyl	−195[b]	9.11
45	CH_3CHOH	Hydroxyethyl	−37[b]	6.7
57	$CH_3C(O)CH_2$	2-Oxopropyl	−39[b]	8.2[b]
57	C_2H_5CO	Propionyl	−31[b]	6.7[b]
57	$CH_3C(OH)CH$	Propen-2-ol-1-yl	111[b]	8.2[b]
57	CH_3CHCOH	Propen-1-ol-1-yl	105[b]	7.0[b]
57	$CH_2C(OH)CH_2$	Propen-2-ol-3-yl	11[b]	7.9[b]
58	$CH_3C(O)CH_3$	Acetone	−218.5	9.70
58	$CH_3C(OH)CH_2$	Propen-2-ol	−176	8.67
72	$CH_3C(O)C_2H_5$	2-Butanone	−238.6	9.52
72	$CH_2C(OH)C_2H_5$	1-Buten-2-ol	−204[b]	8.6
72	$CH_3C(OH)CHCH_3$	2-Buten-2-ol	−214	8.42

[a] From [47].
[b] Calculated.

3. Results and discussion

The cross-sections for the formations of various $C_nH_m^+$ and $C_pH_qO^+$ ions which contribute to more than 90% of the total ionization of acetone and 2-butanone are shown in Figs. 1 and 3 for the two major ions. Figs. 2 and 4 show the cross-sections for the formations of the minor ions of the two ketones. We estimate, according to Section 2, that the uncertainty in the given values is 10% above 20 eV and 20% below 20 eV. The total ionization cross-sections plotted in Figs. 1 and 3 are the sum of all the cross-sections listed in Tables 2 and 5. The total cross-section for ion formation from acetone shows a threshold level at 12 eV, rising up to 40 eV and reaching

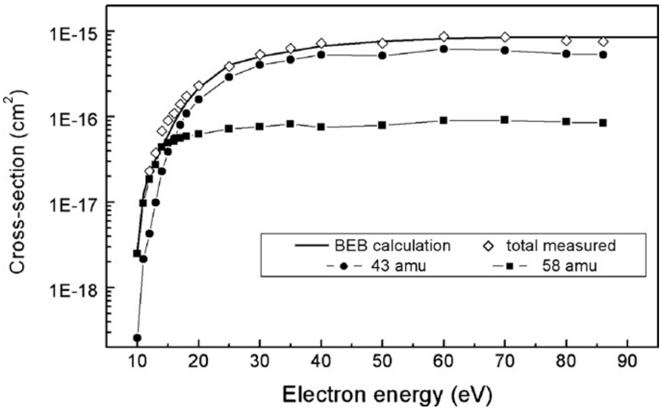

Fig. 1. Total ionization cross-sections for the formation of ions from acetone, measured and calculated. Cross-section for the formation of molecular ion and of 43 amu ion.

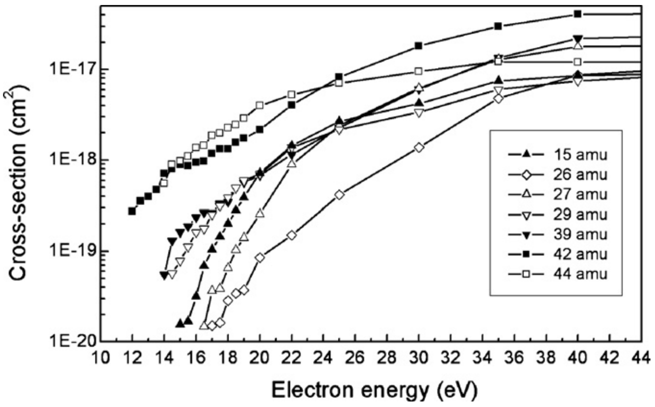

Fig. 2. Cross-sections for the formation of minority ions issued from acetone.

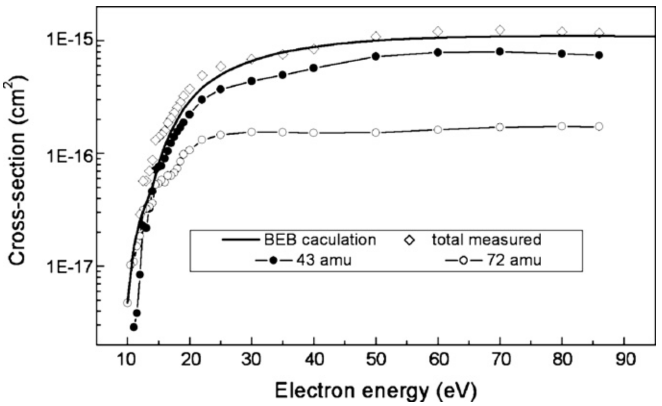

Fig. 3. Total ionization cross-sections for the formation of ions from 2-butanone, measured and calculated. Cross-section for the formation of molecular ion and of 43 amu ion.

a maximum value of 8.7×10^{-16} cm^2 at around 60 eV before a slight decrease until 86 eV, the maximum usable voltage. The total cross-section, for the ion formation from 2-butanone, shows a similar trend with a maximum value of 1.25×10^{-15} cm^2 at 70 eV before a slight decrease.

The measured total cross-section of acetone in Fig. 1 agrees well with the cross-section given by the theoretical model between 12 and 86 eV. The differences between the experimental data and the data given by the model are compatible with the experimental uncertainties mentioned previously. Between 10 eV, just above the ionization threshold of acetone (9.70 eV [13]) and 12 eV, near the threshold of xenon (12.13 eV [31]), only 58 and 43 amu ions are observed. Thus, the cross−section of each of these two ions is calculated in order to normalize the sum to the value given by the BEB model. No significant signal was measured below 10 eV.

The measured total cross-section of 2-butanone in Fig. 3 well agrees with the cross-section given by the theoretical model between 25 and 86 eV, taking into account the experimental uncertainties. Below 25 eV, our results are slightly higher than those given by the BEB model. Between 10 eV, just above the threshold of 2-butanone (9.52 eV [13]) and 12 eV, three ions of 72, 57 and 43 amu are observed. The cross-section of each of these three ions is calculated in order to normalize the sum to the value given by the BEB model. As the BEB model underestimates our experimental results, the cross-sections of these ions may be underestimated in the range 10–12 eV, but this does not change the considerations as to the formation of each of these ions. No signal was measured below 10 eV.

The formation of an appreciable number of ions from acetone and 2-butanone results from primary processes: the kinetic energy resulting from the electron collision is converted into internal energy leading to the dissociation of the ion into a smaller one and a neutral fragment. The fact that the molecular ions are observed over the whole range of ionization energy suggests that the formation of an appreciable number of ions results directly from the fragmentation of the molecular ions via a simple bond splitting process or via a bond splitting followed by H-atom transfer between the two fragments.

In the following, the formation of some ions considered in Table 2 will be explained as the result either of a simple bond splitting of the molecular acetone ion, or of bond splittings followed by rearrangements. It will be tried to understand the formation of the other ions issued from acetone. The same procedure will be followed regarding the formation of some of the ions considered in Table 5 from 2-butanone. Finally, the results of the two ketones will be compared.

3.1. Ions issued from acetone

About thirty different masses are observed but only nine of them have been selected: those whose ionization cross-section is greater than 1×10^{-17} cm^2 at 86 eV (Table 2). The relative cross-sections are larger than 1% of the total cross-section at 86 eV. The 58 amu molecular ion and the principal 43 amu fragment ion contribute to more than 80% of the total cross-section at this maximum voltage, and 99% of the total cross-section at 12 eV. The molecular ion is the most abundant in the 9.7–15 eV range. Seven minor ions (42, 39, 27, 26, 44, 29 and 15 amu) are detected above 17 eV and one of them (42 amu) is present at 12 eV. From 40 to 86 eV, the cross-sections of these minor ions are almost constant. For this reason, the energy range in Fig. 2 is only from 10 to 44 eV in order to show the detail of the cross-sections in the vicinity of the threshold.

3.1.1. The molecular ion

The cross-section for the formation of the 58 amu ion is close to 8×10^{-17} cm^2 between 86 and 25 eV and then decreases clearly to 10 eV, near the ionization threshold. This ion is the major ion below 15 eV.

Since a molecule with the empirical formula of C_3H_6O corresponds to many isomers such as acetone or propene-2-ol, $C_3H_6O^+$ can be described by the corresponding cations. The propene-2-ol ion $CH_3C(OH)CH_2^+$ is observed during the decomposition of 2-ketone cations [32,33] as a result of a two step process. First, an O–H bond is formed with subsequent transfer of this H-atom through a sterically favourable six-membered-ring transition state. The second step is an α-cleavage by a splitting of a C–C bond yielding an enol ion. This mechanism is well known and is usually referred to as the “McLafferty rearrangement” [34,35].

The formation of the acetone cation by electron impact on neutral $CH_3C(O)CH_3$ can be followed by rearrangements of the bonds in the initially ionized molecule, that leads to the propene-2-ol ion [32]. Table 1 shows that the enthalpy of formation of acetone is lower than the one of propene-2-ol but the ionization energy of the enol is lower than the one of the ketone; thus the enol cation ($\Delta_f H^\circ = 661$ kJ mol^{-1}) is more stable than the ketone cation ($\Delta_f H^\circ = 718$ kJ mol^{-1}). A transition state above the ketone cation is estimated theoretically at 151 kJ mol^{-1} (1.56 eV) by Wei et al. [36] and experimentally at 175 ± 27 kJ mol^{-1} (1.81 ± 0.28 eV) by McAdoo [37]. Near the threshold the 58 amu ion must correspond to the acetone cation, and for electron energies above 12 eV the two cations can be present assuming that no dissociation occurs before isomerization. These two species must be taken into account in determining possible fragmentation pathways in the following.

3.1.2. The 43 amu ion

This fragment ion is the major one above 15 eV. The cross-section is close to 5×10^{-16} cm^2 and contributes to 70% of the total cross-section between 86 and 40 eV. At lower energies, its contribution decreases first slowly and then quickly. This ion is still detected at 10 eV, just above the ionization threshold, contributing 10% to the total cross-section.

This ion may be issued from a splitting of one of the two C–C bonds leading to the even numbered electron acetyl ion $CH_3{-}C{\equiv}O^+$ and a methyl radical. Table 3 shows that the dissociations of the molecular ion are endothermic. In the right column of Table 3, values of ΔE give the threshold energy to obtain the ion from neutral acetone via the process considered and using the values of Table 1. Dissociative photoionization of acetone studied by Wei et al. [36] gives an appearance energy (AE) of 10.49 ± 0.02 eV for CH_3CO^+, the threshold photoelectron spectrum of Fogleman et al. [38] shows an onset value of 10.563 ± 0.010 eV and the molecular beam photoionization studied by Trott et al. [39] gives an AE of 10.52 ± 0.01 eV.

Table 2
Cross-sections σ ($\times 10^{-16}$ cm^2) for the formation of the main ions from acetone at 86 eV (maximum voltage used), 25 and 12 eV (near the threshold)

Mass (amu)	86 eV		25 eV		12 eV	
	σ	σ relativity (%)	σ	σ relativity (%)	σ	σ relativity (%)
43	5.3	70	3.0	74	0.056	14
58	0.84	11	0.80	20	0.34	85
42	0.45	5.9	0.082	2.0	0.003	0.80
39	0.26	3.4	0.023	0.57	–	–
27	0.21	2.8	0.024	0.59	–	–
26	0.16	2.1	0.004	0.10	–	–
44	0.14	1.8	0.070	1.6	–	–
29	0.12	1.6	0.022	0.54	–	–
15	0.10	1.3	0.027	0.67	–	–

Ions are listed in order of decreasing cross-section for 86 eV.

These values are very close to the ΔE of reaction (1) in Table 3 and are just above 10 ± 0.5 eV, the minimum voltage for which this ion is observed in our study.

Assuming that the propene-2-ol cation is present, i.e., the transition state for isomerization is crossed before dissociative reaction (1) occurs, this enol cation can dissociate yielding an even-electron cation $CH_2{=}C{=}OH^+$ (vinyl oxide) and a methyl radical. It has been shown [40] that about 1% of the total $C_2H_3O^+$ daughter ions from 70 eV electron-impact-ionization have this structure and are formed by the dissociation of the enol cation. Table 3 shows that the ΔE to obtain this ion from acetone by reaction (2) is 1.9 eV higher than that of reaction (1).

A third isomer noted c-$C_2H_3O^+$, substantially higher in energy than the others ($\Delta_f H^\circ = 887$ kJ mol^{-1}), probably has a cyclic structure as suggested by Wei et al. [36]. The AE measured for the formation of this ion and a CH_3 radical is 12.82 ± 0.03 eV, thus ΔE of reaction (3) is 2.4 eV above reaction (1). Hence, this species may be present above 13 eV.

3.1.3. *The 42 amu ion*

The cross-section for the formation of this ion is close to 4×10^{-17} cm^2 between 86 and 40 eV and then decreases slowly to 12 eV, the minimum voltage used corresponding to the threshold of the xenon. The formation of the odd-electron ketene ion $CH_2{=}C{=}O^{\bullet +}$ from the acetone cation is well described by Wei et al. [36] using ab initio calculations. The molecular ion first undergoes a process of C–C bond cleavage via an ion-radical complex; then a methyl migration followed by a hydrogen abstraction produces CH_2CO^+ and CH_4. An AE of 10.53 ± 0.02 eV was measured by these authors. Table 3 shows that the ΔE to obtain this ion from acetone by the reaction (4) is 10.6 eV, the same as for the reaction (1) with the loss of the methyl. Another dissociation channel could produce CH_2CO^+: the ketene ion can be formed via the loss of a hydrogen atom from the acetyl cation, the neutral products would then be CH_3 and an H-atom. The AE measured in the dissociative photoionization of acetone [36] is found to be 14.97 ± 0.04 eV and the ΔE to obtain this ion from acetone by the reaction (5) is 15.2 eV. However, the minimum voltage for which this ion is here observed is 12 eV (Fig. 2). This would imply that the formation of the ketene ion must be described by the reaction (4) below 15 eV and by reactions (4) and (5) for higher energies.

The mean value for the C=O bond enthalpy is about 7.7 eV [13], and is larger than those of the C–C bond enthalpy (3.6 eV) and of the C–H bond enthalpy (4.5 eV). Assuming that reactions (4) and (5) are the result of the splitting of two bonds, a single bond cleavage between the middle carbon and oxygen can be considered, yielding a neutral O atom and the propene cation via a H-atom rearrangement. The ΔE of 14.8 eV for the reaction (6) once again seems to indicate that the formation of the ion of 42 amu must be described by the reaction (4) at low energy.

3.1.4. *The 39 amu ion*

The cross-section for the formation of this ion is close to 2.5×10^{-17} cm^2 between 86 and 40 eV and then decreases slowly to 14 ± 0.5 eV. The ion is not observed at lower energy. An AE of 14.51 ± 0.03 eV for $C_3H_3{}^+$ was measured by Wei et al. [36]. Two isomeric structures can be considered for this cation: the linear propargyl ion l-$C_3H_3{}^+$ and the cyclopropenyl ion c-$C_3H_3{}^+$. They

Table 3
Dissociation reactions with the molecular ions of acetone

Molecular ion $OE^{+\bullet} \rightarrow$ ion	Neutral	$\Delta_r H^\circ$ (kJ mol^{-1})	ΔE (eV)
$CH_3C(O)CH_{3(58)}{}^+ \rightarrow CH_3CO_{(43)}{}^+$ (1)	$CH_{3(15)}$	92	10.6
$CH_3C(O)CH_{3(58)}{}^+ \rightarrow CH_2COH_{(43)}{}^+$ (2)	$CH_{3(15)}$	266	12.5
$CH_3C(O)CH_{3(58)}{}^+ \rightarrow c\text{-}C_2H_3O_{(43)}{}^+$ (3)	$CH_{3(15)}$	315	13.0
$CH_3C(O)CH_{3(58)}{}^+ \rightarrow CH_2CO_{(42)}{}^+$ (4)	$CH_{4(16)}$	89	10.6
$CH_3C(O)CH_{3(58)}{}^+ \rightarrow CH_2CO_{42)}{}^+$ (5)	$CH_3 + H_{(16)}$	527	15.2
$CH_3C(O)CH_{3(58)}{}^+ \rightarrow CH_3CHCH_{2(42)}{}^+$ (6)	$O_{(16)}$	491	14.8
$CH_3C(O)CH_{3(58)}{}^+ \rightarrow c\text{-}C_3H_{3(39)}{}^+$ (7)	$H_2O + H_{(19)}$	338	13.2
$CH_3C(O)CH_{3(58)}{}^+ \rightarrow l\text{-}C_3H_{3(39)}{}^+$ (8)	$H_2O + H_{(19)}$	434	14.2
$CH_3C(O)CH_{3(58)}{}^+ \rightarrow C_2H_{3(27)}{}^+$ (9)	$CH_3O_{(31)}$	395	13.8
$CH_3C(O)CH_{3(58)}{}^+ \rightarrow C_2H_{3(27)}{}^+$ (10)	$CH_2OH_{(31)}$	369	13.5
$CH_3C(O)CH_{3(58)}{}^+ \rightarrow C_2H_{2(26)}{}^+$ (11)	$CH_3OH_{(32)}$	408	13.9
$CH_3C(O)CH_{3(58)}{}^+ \rightarrow CH_3CHO_{(44)}{}^+$ (12)	$CH_{2(14)}$	488	14.7
$CH_3C(O)CH_{3(58)}{}^+ \rightarrow CH_2CHOH_{(44)}{}^+$ (13)	$CH_{2(14)}$	436	14.2
$CH_3C(O)CH_{3(58)}{}^+ \rightarrow HCO_{(29)}{}^+$ (14)	$C_2H_{5(29)}$	229	12.1
$CH_3C(O)CH_{3(58)}{}^+ \rightarrow C_2H_{5(29)}{}^+$ (15)	$HCO_{(29)}$	229	12.1
$CH_3C(O)CH_{3(58)}{}^+ \rightarrow CH_{3(15)}{}^+$ (16)	$CH_3CO_{(43)}$	366	13.5
$CH_3C(O)CH_{3(58)}{}^+ \rightarrow CH_{3(15)}{}^+$ (17)	$CH_2COH_{(43)}$	511	15.0
$CH_3C(O)CH_{3(58)}{}^+ \rightarrow CH_{3(15)}{}^+$ (18)	$c\text{-}C_2H_3O_{(43)}$	540	15.3

Masses (in parentheses) are given in amu.

result from losses of H_2O and a H-atom from the molecular ion. The ΔE of reaction (7) in Table 3 is clearly lower than the measured AE whereas that of reaction (8) is close to Wei's experimental value. It seems that the formation of both structures are possible in this work and thus the ion of 39 amu may be described as the propargyl and the cyclopropenyl ions issued from reactions (7) and (8).

3.1.5. The 27 amu ion$^+$

This ion has a cross-section of 2×10^{-17} cm^2 from 86 to 40 eV which decreases slowly at lower energies. The ion is not observed below 16.5 ± 0.5 eV. It may be regarded as the vinyl cation. Wei et al. [36] have measured a slightly lower AE of 15.59 ± 0.04 eV. The ion results from the loss either of a methoxyl radical in reaction (9) or of a hydroxymethyl radical in reaction (10). The ΔE of both reactions are clearly lower than the measured AE, but Stevenson's rule, which stipulates that the fragment of lowest ionization energy retains the charge and becomes the ionic fragment, appears not to be respected in reaction (10) (see the IE values of Table 1). This consideration allows to conclude that the vinyl cation is issued from reaction (9) with the loss of a methoxyl radical.

The dissociation of the acetyl cation, the major fragment ion above 15 eV, can also yield the vinyl cation, via the loss of the oxygen atom and a H-atom rearrangement. Table 4 shows that the ΔE of reaction (19) is 17.7 eV and the 27 amu ion can be issued from the dissociation of the acetyl ion above this energy. The dissociation of the propene cation via reaction (20) can also yield, with the same ΔE, the vinyl cation but since propene is a minority ion, the formation of vinyl ion via reaction (20) is very weak.

The bridged hydrogen form of the vinyl cation has been considered to have a theoretical enthalpy of formation 0.26 eV lower than the classical vinyl cation [41]. Moreover, an ionization energy 0.34 eV higher [42,43] than the one given by the NIST [13] has been measured for the vinyl radical. This can lead to uncertainty of 0.6 eV in the ΔE of reactions (9), (10), (19) and (20) but that does not change the conclusions of the two preceding paragraphs.

3.1.6. The 26 amu ion

The acetylene cation has a cross-section of 1.5×10^{-17} cm^2 above 50 eV and then decreases slowly at lower energies. It is not observed below 17 eV and has the lowest measured cross-section of the nine reported ions below 35 eV. Dissociation of the molecular ion by reaction (11) can lead, after one C–C and one C=O bond split followed by H-atom rearrangement, to $C_2H_2^+$ and a neutral which could be methanol, but again Stevenson's rule is not respected. The formation of other neutrals such CH_4 with an O atom leads to a ΔE larger than 18 eV. The dissociation of CH_2CO^+ can also yield $C_2H_2^+$ according to Stevenson's rule and since the ΔE of reaction (21) is slightly more than 17 ± 0.5 eV, it is possible that the acetylene cation results from reaction (21).

3.1.7. The 44 amu ion

The cross-section for the formation of this ion is close to 1.5×10^{-17} cm^2 between 86 and 35 eV and then decreases slowly to 14 eV. This ion may result from two pathways: (i) the loss of a methyl group of the molecular ion followed by H-atom rearrangement between the two fragments, yielding acetaldehyde ion CH_3CHO^+ by reaction (12), (ii) the loss of the methyl group from the propene-2-ol ion followed by H-atom rearrangement between the two fragments, yielding the ethenol ion CH_2CHOH^+ by reaction (13). The ΔE of reactions (12) and (13) in Table 3 is slightly higher than 14 ± 0.5 eV.

The formation of a third isomer, a cyclic ethylene oxide, is not considered possible because it requires a ΔE of 16.3 eV, clearly higher than our measured threshold of 14 eV.

3.1.8. The 29 amu ion

The cross-section for the formation of this ion decreases slowly from 50 to 14.5 eV. This ion can be described as either the ethyl cation or the formyl cation. Reactions (14) and (15) need the same enthalpy and the ΔE for the formation of the ionic species from the neutral acetone are similar and lower than 14.5 eV, assuming that the neutral species formed are formyl and ethyl radicals. It is not easy to choose the correct reaction pathway yielding the 29 amu ion since the two possible ions have the same ionization energy. Theoretical calculations by Wei et al. [36] suggest that propene-2-ol cation can lead, via a first transition state with a 3-carbon cycle and a second transition state with a COH cycle, to the stable ion $CH_3{-}CH_2{-}HC{=}O^{\bullet+}$. Then, a C–C bond split can occur, leading to the ethyl and formyl species. It is to be expected that the charged site remains on the oxygen, thus, with its stabilizing triple C≡O bond, the formation of the formyl cation is favoured instead of that of the ethyl cation. It must be stated that HCO^+ was formally identified in multiphoton ionization study of deuterated acetone by Majumder et al. [44].

The dissociation of the minority propene cation via reaction (22) leads to a high ΔE which suggests that the ethyl cation cannot be issued from propene at low energy.

3.1.9. The 15 amu ion

With a cross-section of 10^{-17} cm^2, CH_3^+ is the minority ion among the nine measured ions between 86 and 45 eV. At lower energy, its cross-section decreases but less slowly than those of the other ions in Fig. 2: between 25 and 20 eV, the cross-section of CH_3^+ is higher than those of the 26, 27, 29 and 39 amu ions. This ion is not detected below 15 ± 0.5 eV. An AE of 14.41 ± 0.04 eV was measured in the dissociative photoionization of acetone [36]. The ΔE of reactions (16) in Table 3 is lower than this AE whereas the ΔE of reactions (17) and (18) are higher. It should be noted that Stevenson's rule is again not respected in these last three reactions so that the methyl ion may not result directly from dissociation of the molecular ion.

The dissociation of the acetyl ion CH_3CO^+ by reaction (23) in Table 4 leads to a ΔE lower than the measured AE and here, it is in agreement with Stevenson's rule. The dissociations of CH_2COH^+ and c-$C_2H_3O^+$ into the same fragments CH_3^+ and CO have the same threshold. Since ion of 43 amu is the majority ion above 15 eV, the observed methyl ion can result from the dissociation of a fragment of 43 amu ion rather than from the direct dissociation of the molecular ion [45]. A similar conclusion is given by Apicella et al. [46] in the mass spectrometric study of deuterated methyl *t*-butyl in which methyl ion can be formed by a primary process as well as by a lot of secondary processes.

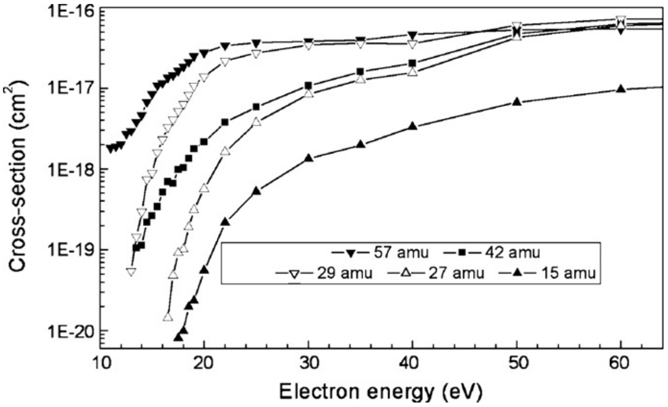

Fig. 4. Cross-sections for the formation of minority ions issued from 2-butanone.

Table 4
Dissociation reactions of the fragment ions

Parent ion → ion	Neutral	$\Delta_r H^\circ$ (kJ mol^{-1})	ΔE (eV) (from acetone)	ΔE (eV) (from 2-butanone)
$CH_3CO_{(43)}{}^+ \rightarrow C_2H_{3(27)}{}^+$ (19)	$O_{(16)}$	681	17.7	17.7
$CH_3CHCH_{2(42)}{}^+ \rightarrow C_2H_{3(27)}{}^+$ (20)	$CH_{3(15)}$	281	17.7	21.9
$CH_2CO_{(42)}{}^+ \rightarrow C_2H_{2(26)}{}^+$ (21)	$O_{(16)}$	694	17.7	17.8
$CH_3CHCH_{2(42)}{}^+ \rightarrow C_2H_{5(29)}{}^+$ (22)	$CH_{(13)}$	538	20.4	24.6
$CH_3CO_{(43)}{}^+ \rightarrow CH_{3(15)}{}^+$ (23)	$CO_{(28)}$	321	13.9	13.9
$C_2H_5CO_{(57)}{}^+ \rightarrow C_2H_{5(29)}{}^+$ (24)	$CO_{(28)}$	177	–	12.2

Masses (in parentheses) are given in amu.

3.2. *Ions issued from 2-butanone*

Fifteen different masses are observed in the spectrum of 2-butanone but only seven of them, with ionization cross-section greater than 1×10^{-17} cm^2 at 86 eV (Table 5), have been selected. The relative cross-sections are at least 1% of the total cross-section at 86 eV. The 72 amu molecular ion and the 43 amu fragment ion contribute to about 80% of the total cross-section between 86 and 25 eV, and 94% of the total cross-section at 12 eV. The molecular ion is the most abundant in the 9.52–13.5 eV range. Five minor ions (42, 29, 27, 57 and 15 amu) are detected above 17.5 eV and the 57 amu ion is present at 12 eV. From 60 to 86 eV, the cross−sections are almost constant so Fig. 4 is plotted with energy scale between 10 and 65 eV to show more detail.

3.2.1. *The molecular ion*

The cross-section for the formation of the 72 amu ion is constant and equal to 1.7×10^{-17} cm^2 between 86 and 30 eV and then decreases as the energy drops to 10 eV, near the ionization threshold. This ion is the majority one below 13.5 eV.

The formation of the 2-butanone cation can be followed, via a transition state with a four-membered ring, by a H-atom rearrangement between one of the α-C atoms and the O atom. This yields the two enol ions of 2-butanone: 1-buten-2-ol and 2-buten-2-ol (E and Z). Isomerization between the enol and keto ions has been widely studied [47–51]. Table 1 shows that the enthalpy of formation of 2-butanone is lower than those of the two enols but the ionization energies of the enols are lower than that of the ketone; thus the two enol cations ($\Delta_f H^\circ = 626$ kJ mol^{-1} for 1-buten-2-ol and 599 kJ mol^{-1} for 2-buten-2-ol) are more stable than the ketone cation ($\Delta_f H^\circ = 680$ kJ mol^{-1}). Assuming a transition state between the 2-butanone and the two enols similar to that for acetone, the 72 amu ion can be identified as the cation of 2-butanone near the threshold. For electron energies above 12 eV, it can be supposed that the two enol ions could be present if no dissociation occurs before isomerization.

3.2.2. *The 43 amu ion*

This ion is the most abundant above 14 eV. The cross-section reaches a maximum value of 8×10^{-16} cm^2 at 70 eV, contributing to 70% of the total cross-section, decreasing slowly until 25 eV and quickly to 11 eV. This ion is not observed at lower energy whereas it is detected at 10 eV with acetone.

This ion may be issued from a C–C bond cleavage leading to even-electron acetyl ion and an ethyl radical. Table 6 shows that the dissociations of the 2-butanone cation are endothermic. The values of ΔE in the right column give the threshold energy for obtaining the ion from the neutral 2-butanone via the process considered, using the values in Table 1. The threshold energy for reaction (25) is consistent with the photoionization appearance energy (10.40 eV) measured by Griffin et al. [52] and the smallest energy (11 eV) for which the 43 amu ion is detected.

Assuming that the 1-buten-2-ol cation is present, it can dissociate to the vinyl oxide cation and an ethyl radical. Table 6 shows that ΔE for obtaining this ion from 2-butanone by reaction (26) is 1.8 eV above the ΔE of reaction (25). The ΔE for obtaining the cyclic oxiranyl cation by reaction (27) is 2.3 eV above the ΔE of reaction (25). Thus, these two cations may be present above 13 eV.

3.2.3. *The 42 amu ion*

The cross-section for the formation of this ion, 5.6×10^{-17} cm^2 is constant in the 86–50 eV range and decreases slowly until 13.5 eV. The ion is not observed at lower energy whereas it is detected at 12 eV with acetone.

Reactions similar to reactions (4) and (5) can lead to an odd-electron ketene ion and a neutral species: ethane via reaction (28), ethyl and atomic hydrogen via reaction (29). A C═O bond cleavage and a H-atom rearrangement can lead to the formation of the propene cation, methylene and atomic oxygen in reaction (30). As reaction (29) doesn't respect Stevenson's rule and the ΔE for reaction (30) is 19 eV, it seems that the 42 amu ion can be described at low energy as $CH_2{=}C{=}O^{\bullet+}$, issued from reaction (28).

3.2.4. *The 29 amu ion*

The cross-section for the formation of this ion represents about 5% of the total cross-section between 86 and 25 eV and then decreases as the energy drops to 13 eV. This measured threshold is lower than the one measured with acetone (14.5 eV). Reaction (31) can lead, via a mechanism similar to that described in reactions (14) and (15), to $CH_3{-}CH_2{-}CH_2{-}HC{=}O^{\bullet+}$. This ion can further dissociate

Table 5
Cross-sections σ ($\times 10^{-16}$ cm^2) for the formation of the main ions from 2-butanone at 86 eV (maximum voltage used), 25 and 12 eV (near the threshold)

Mass (amu)	86 eV		25 eV		12 eV	
	σ	σ relativity (%)	σ	σ relativity (%)	σ	σ relativity (%)
43	7.4	64	3.7	62	0.084	29
72	1.7	15	1.5	25	0.19	65
42	0.66	5.6	0.058	1.0	–	–
29	0.62	5.3	0.27	4.6	–	–
27	0.62	5.3	0.038	0.64	–	–
57	0.52	4.4	0.39	6.5	0.020	6.0
15	0.11	1.0	0.005	0.09	–	–

Ions are listed in order of decreasing cross-section for 86 eV.

Table 6
Dissociation reactions with the molecular ion of 2-butanone

Molecular ion OE$^{+\bullet}$ → ion		Neutral	Δ_rH° (kJ mol^{-1})	ΔE (eV)
$CH_3C(O)C_2H_{5(72)}{}^+ \rightarrow CH_3CO_{(43)}{}^+$	(25)	$C_2H_{5(29)}$	102	10.6
$CH_3C(O)C_2H_{5(72)}{}^+ \rightarrow CH_2COH_{(43)}{}^+$	(26)	$C_2H_{5(29)}$	277	12.4
$CH_3C(O)C_2H_{5(72)}{}^+ \rightarrow c\text{-}C_2H_3O_{(43)}{}^+$	(27)	$C_2H_{5(29)}$	326	12.9
$CH_3C(O)C_2H_{5(72)}{}^+ \rightarrow CH_2CO_{(42)}{}^+$	(28)	$C_2H_{6(30)}$	118	10.7
$CH_3C(O)C_2H_{5(72)}{}^+ \rightarrow CH_2CO_{(42)}{}^+$	(29)	$C_2H_5 + H_{(30)}$	538	15.1
$CH_3C(O)C_2H_{5(72)}{}^+ \rightarrow CH_3CHCH_{2(42)}{}^+$	(30)	$O + CH_{2(30)}$	915	19.0
$CH_3C(O)C_2H_{5(72)}{}^+ \rightarrow HCO_{(29)}{}^+$	(31)	$n\text{-}C_3H_{7(43)}$	247	12.1
$CH_3C(O)C_2H_{5(72)}{}^+ \rightarrow C_2H_{5(29)}{}^+$	(32)	$CH_3CO_{(43)}$	211	11.7
$CH_3C(O)C_2H_{5(72)}{}^+ \rightarrow HCO_{(29)}{}^+$	(33)	$CH_3 + C_2H_{4(43)}$	345	13.1
$CH_3C(O)C_2H_{5(72)}{}^+ \rightarrow C_2H_{3(27)}{}^+$	(34)	$C_2H_5O_{(45)}$	220	11.8
$CH_3C(O)C_2H_{5(72)}{}^+ \rightarrow C_2H_{3(27)}{}^+$	(35)	$CH_3CHOH_{(45)}$	378	13.4
$CH_3C(O)C_2H_{5(72)}{}^+ \rightarrow CH_3C(O)CH_{2(57)}{}^+$	(36)	$CH_{3(15)}$	218	11.8
$CH_3C(O)C_2H_{5(72)}{}^+ \rightarrow C_2H_5CO_{(57)}{}^+$	(37)	$CH_{3(15)}$	82	10.4
$CH_3C(O)C_2H_{5(72)}{}^+ \rightarrow CH_3C(OH)CH_{(57)}{}^+$	(38)	$CH_{3(15)}$	368	13.3
$CH_3C(O)C_2H_{5(72)}{}^+ \rightarrow C_2H_4COH_{(57)}{}^+$	(39)	$CH_{3(15)}$	246	12.1
$CH_3C(O)C_2H_{5(72)}{}^+ \rightarrow CH_2C(OH)CH_{2(57)}{}^+$	(40)	$CH_{3(15)}$	239	12.0
$CH_3C(O)C_2H_{5(72)}{}^+ \rightarrow CH_{3(15)}{}^+$	(41)	$CH_3C(O)CH_{2(57)}$	376	13.4
$CH_3C(O)C_2H_{5(72)}{}^+ \rightarrow CH_{3(15)}{}^+$	(42)	$C_2H_5CO_{(57)}$	384	13.5
$CH_3C(O)C_2H_{5(72)}{}^+ \rightarrow CH_{3(15)}{}^+$	(43)	$CH_3C(OH)CH_{(57)}$	526	15.0
$CH_3C(O)C_2H_{5(72)}{}^+ \rightarrow CH_{3(15)}{}^+$	(44)	$C_2H_4COH_{(57)}$	520	14.9
$CH_3C(O)C_2H_{5(72)}{}^+ \rightarrow CH_{3(15)}{}^+$	(45)	$CH_2C(OH)CH_{2(57)}$	426	13.9

Masses (in parentheses) are given in amu.

into the formyl cation and propyl radical. Reaction (32) can lead, via a simple C–C split in the molecular ion, to the ethyl cation and acetyl radical. The IE in Table 1 indicates that again Stevenson's rule is not respected in these reactions. Thus, the formyl and ethyl cations may not result directly from dissociation of the molecular ion. Another dissociation channel could produce formyl cation: the cation formed via the previous mechanism can loose successively a methyl radical and later C_2H_4. Reaction (33) respects Stevenson's rule and gives value of ΔE consistent with our measured threshold of 13 eV.

The dissociation of the propanoyl cation via reaction (24) leads to a low ΔE, but as propanoyl is a minority ion, the formation of the ethyl cation via reaction (24) is very weak. The dissociation of the minority propene via reaction (22) may not be possible at low energy.

3.2.5. *The 27 amu ion*

The cross-section for the formation of this ion is the same as those of the 42 and 29 amu ions between 86 and 50 eV but the cross-section decreases more quickly than that of the two previous ions. $C_2H_3{}^+$ is not observed below 16.5 eV, as with acetone. The loss of an ethoxyl radical in reaction (34) or a hydroxyethyl radical in reaction (35) leads to the formation of the vinyl cation. The ΔE are weaker than the measured threshold of 16.5 eV but reaction (35) does not respect Stevenson's rule, so that thus, the vinyl cation is issued from reaction (34) with the formation of an ethoxyl radical.

As with acetone, the dissociation of the acetyl cation, the majority fragment ion above 14 eV, can also lead to the vinyl cation with the same ΔE of 17.7 eV as in reaction (19). The dissociation of the minority propene cation via reaction (20) with a ΔE of 21.9 eV can also lead to the vinyl cation at higher energy but this pathway is very weak.

3.2.6. *The 57 amu ion*

The cross-section for the formation of this ion is close to 5×10^{-17} cm^2 in the 86–25 eV range and then decreases slowly as the energy drops to 11 eV. As for the 43 amu ion, it is not observed at lower energy. This ion becomes the most important of the five minor fragment ions below 50 eV. It is issued from a C–C bond cleavage leading to $C_3H_5O^+$ and a methyl radical. Table 6 shows that the dissociations of 2-butanone can occur via the loss of the methyl from the carbon C4 in reaction (36) or the loss of the methyl from the carbon C1 in reaction (37). Assuming that the 2-buten-2-ol cation is present, it can dissociate by losing a methyl from the carbon C4 in reaction (38) or from the carbon C1 in reaction (39). Assuming that the 1-buten-2-ol cation is present, it can dissociate by losing the methyl from the carbon C4 in reaction (40). Among these five reactions, only the ΔE of reaction (37), which is the least endothermic, is consistent with the photoionization appearance energy measured by Griffin et al. [52] (10.20 eV) and the smallest energy (11 eV) at which we detect the ion. Thus, near the threshold, $C_3H_5O^+$ can be described as an odd-electron propionyl cation. The 57 amu ion may be generated from the four other reactions at higher energy.

It is interesting to compare the formations of $C_2H_3O^+$ and $C_3H_5O^+$ from the 2-butanone cation. Both proceed via an α-cleavage and have the same detection threshold of 11 eV. The ratio $[C_2H_3O^+]/[C_3H_5O^+]$ is close to 15 at 70 eV and 10 at 25 eV, but decreases to 1.5 at 11 eV. It seems that near the threshold, the loss of the smaller alkyl is favoured with respect to the loss of the larger alkyl, this trend being reversed when the energy increases. The effects of fragment size have been investigated many years ago [33,53,54]. Experimental and theoretical studies of Griffin et al. [52] have shown that the loss of the larger alkyl is favoured by the lengthened C–C bond when different alkyl substituents are present.

3.2.7. *The 15 amu ion*

The cross-section for the formation of the methyl ion is close to 10^{-17} cm^2, as for acetone, between 86 and 60 eV and then decreases slowly to 17.5 eV. The ion is not observed at lower energy whereas it is detected at 15 eV with acetone. $CH_3{}^+$ is the minority ion among the seven measured ions over the energy range used. Reactions (41)–(45) can lead to the formation of the methyl ion and a neutral species corresponding to the five 57 amu ions. The ionization energies in Table 1 show that Stevenson's rule is not respected in these five reactions. As for acetone, the methyl ion may not result directly from dissociation of the molecular ion.

The dissociation of the acetyl ion CH_3CO^+ via reaction (23) in Table 3 leads to a ΔE lower than 17.5 eV. The dissociations of CH_2COH^+ and $c\text{-}C_2H_3O^+$ into the same fragments $CH_3{}^+$ and CO have to the same ΔE. The ion of 43 amu being the majority ion above 14 eV, implies that the observed methyl ion could result, as for acetone, from the dissociation of a 43 amu fragment ion.

4. Conclusion

The electron impact ionization of acetone and 2-butanone produces molecular ions and fragment ions. The cross-sections for the formation of the major species are measured between 10 and 86 eV. The present results are in good agreement with total ionization cross-sections measured and obtained from the BEB theory. For the two ketones, the two molecular ions and the 43 amu ion contribute to about 80% of the total cross-section at 86 eV. The ion of 43 amu is the majority ion above 15 eV; it results from an α-cleavage in the molecular ions. Near the thresholds, the ion of 43 amu is identified as the acetyl cation but two isomers may be present at higher energies. In the case of acetone, an ion of 42 amu is detected in 12–86 eV range and contributes to about 6% of the total cross-section at the maximum voltage used, at low energy it is identified as the ketene cation. Six other minor ions (39, 27, 26, 44, 29 and 15 amu) are detected above 17 eV. Five of them may result from dissociation reactions of the molecular ion and the methyl cation is issued from the majority fragment ion of 43 amu. In the case of 2-butanone, a 57 amu ion is detected from 11 to 86 eV and contributes to about 6% of the total cross-section over the whole range of ionization energy, it may be identified near the threshold as the propionyl cation. The 43 amu and the 57 amu ions both result from an α-cleavage and the effects of fragment size, which favour the formation of the heavier one near the threshold and of the lighter one at higher energy. Four other minor ions (42, 29, 27 and 15 amu) are detected above 18 eV and similar conclusions to those with acetone can be assumed about their formation.

Acknowledgment

The authors are grateful to Andrew Mayne (L.P.P.M. Orsay) for the helpful suggestion and improvement of the English language.

References

[1] S. Szopa, B. Aumont, S. Madronich, Atmos. Chem. Phys. 5 (2005) 2519.
[2] R. Atkinson, Atmos. Environ. 34 (2000) 2063.
[3] R. Atkinson, J. Arey, Chem. Rev. 103 (2003) 4605.
[4] K. Vercammen, A. Berezin, J. Adv. Oxid. Technol. 2 (1997) 312.
[5] H.-H. Kim, Plasma Process. Polym. 1 (2004) 91.
[6] S. Pasquiers, C. Postel, L. Magne, V. Puech, G. Lombardi, J. Adv. Oxid. Technol. 7 (2004) 108.
[7] O. Sarroukh, F. Jorand, C. Postel, L. Magne, S. Pasquiers, Proceedings of the XVIth International Conference on Gas Discharges and their Applications, vol. 1, Xi'an, Chine, September 11–15, 2006, pp. 417–420.
[8] O. Sarroukh, F. Jorand, L. Magne, C. Postel, S. Pasquiers, Proceedings of the Fifth International Symposium of Non-Thermal Plasma Technology for Pollution Control and Sustainable Development (ISNTPT-5), St. Pierre d'Oléron, France, June 19–23, 2006, Abstracts p. 18 + CD-ROM.
[9] K. Bouamra, J.R. Vacher, F. Jorand, N. Simiand, S. Pasquiers, Chem. Phys. Lett. 373 (2003) 237.
[10] J.R. Vacher, N. Blin-Simiand, F. Jorand, S. Pasquiers, Int. J. Mass Spectrom. 240 (2005) 161.
[11] J.R. Vacher, F. Jorand, N. Blin-Simiand, S. Pasquiers, Chem. Phys. 323 (2006) 587.
[12] J.R. Vacher, F. Jorand, N. Blin-Simiand, S. Pasquiers, Chem. Phys. Lett. 434 (2007) 188.
[13] NIST Database, Available at http://webbook.nist.gov/chemistry/. Original References for Data Can be Obtained from this Database.
[14] R.C. Wetzel, F.A. Baiocchi, T.R. Hayes, R.S. Freund, Phys. Rev. A 35 (1987) 559.
[15] D. Rapp, P. Englander-Golden, J. Chem. Phys. 43 (1965) 1464.
[16] K. Stephan, T.D. Märk, J. Chem. Phys. 81 (1984) 3116.
[17] E. Krishnakumar, S.K. Srivastava, J. Phys. B 21 (1988) 1055.
[18] R. Rejoub, B.G. Lindsay, R.F. Stebbings, Phys. Rev. A 65 (2002) 42710.
[19] C.E. Berry, Phys. Rev. 78 (1950) 597.
[20] C. Tian, C.R. Vidal, J. Phys. B 31 (1998) 5369.
[21] H.C. Straub, P. Renault, B.G. Lindsay, K.A. Smith, R.F. Stebbings, Phys. Rev. A 52 (1995) 1115.
[22] C.Q. Jiao, R. Nagpal, P.D. Haaland, Chem. Phys. Lett. 269 (1997) 117.
[23] C.Q. Jiao, C.A. DeJoseph Jr., A. Garscadden, J. Chem. Phys. 114 (2001) 2166.
[24] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford, CT, 2004.
[25] Y.K. Kim, M.E. Rudd, Phys. Rev. A 50 (1994) 3954.
[26] W. Hwang, Y.K. Kim, M.E. Rudd, J. Chem. Phys. 104 (1996) 2956.
[27] M.A. Ali, Y.K. Kim, W. Hwang, N.M. Weinberger, M.E. Rudd, J. Chem. Phys. 106 (1997) 9602.
[28] P.D. Haaland, C.Q. Jiao, A. Garscadden, Chem. Phys. Lett. 340 (2001) 479.
[29] H. Deutsch, K. Becker, S. Matt, T.D. Märk, Int. J. Mass Spectrom. 197 (2000) 37.
[30] C.Q. Jiao, A. Garscadden, P.D. Haaland, Chem. Phys. Lett. 310 (1999) 52.
[31] J.C. Traeger, R.G. McLoughlin, A.J.C. Nicholson, J. Am. Chem. Soc. 104 (1982) 5318.
[32] F.W. McLafferty, D.J. McAdoo, J.S. Smith, R. Kornfeld, J. Am. Chem. Soc. 93 (1971) 3720.
[33] C. Lifshitz, J. Phys. Chem. 87 (1983) 2304.
[34] F.W. McLafferty, Anal. Chem. 28 (1956) 306.
[35] D.G.I. Kingston, J.T. Bursey, M.M. Bursey, Chem. Rev. 74 (1974) 215.
[36] L. Wei, B. Yang, R. Yang, C. Huang, J. Wang, X. Shan, L. Sheng, Y. Zhang, F. Qi, C.-S. Lam, W.-K. Li, J. Phys. Chem. A 109 (2005) 4231.
[37] D.J. McAdoo, Mass Spectrom. Rev. 19 (2000) 38.
[38] E.A. Fogleman, H. Koizumi, J.P. Kercher, B. Sztáray, T. Baer, J. Phys. Chem. A 108 (2004) 5288.
[39] W.M. Trott, N.C. Blais, E.A. Walters, J. Chem. Phys. 69 (1978) 3150.
[40] P.C. Burgers, J.L. Holmes, J.E. Szulejko, A.A. Mommers, J.K. Terlouw, Org. Mass Spectrom. 18 (1983) 254.
[41] M.N. Glukhovtsev, R.D. Bach, Chem. Phys. Lett. 286 (1998) 51.
[42] J. Berkowitz, C.A. Mayhew, B. Ruščić, J. Chem. Phys. 88 (1988) 7396.
[43] M.W. Crofton, M.F. Jagod, D.D. Rehfuss, T. Oka, J. Chem. Phys. 91 (1989) 5139.
[44] C. Majumber, O.D. Jayakumar, R.K. Vasta, S.K. Kulshreshtha, J.P. Mittal, Chem. Phys. Lett. 304 (1999) 51.
[45] J.P. Stadelmann, Chem. Phys. Lett. 89 (1982) 174.
[46] B. Apicella, T.M. Di Palma, X. Wang, R. Velotta, M. Armenante, N. Spinelli, Int. J. Mass Spectrom. 262 (2007) 105.
[47] T.H. Osterheld, J.I. Brauman, J. Am. Chem. Soc. 115 (1993) 10311.
[48] D.J. McAdoo, F.W. McLafferty, J.S. Smith, J. Am. Chem. Soc. 92 (1970) 6343.
[49] D.J. McAdoo, F.W. McLafferty, T.E. Parks, J. Am. Chem. Soc. 94 (1972) 1601.
[50] G. Bouchoux, Mass Spectrom. Part I 7 (1988) 1.
[51] F. Tureček, C.J. Cramer, J. Am. Chem. Soc. 117 (1995) 12243.
[52] L.L. Griffin, J.C. Traeger, C.E. Hudson, D.J. McAdoo, Int. J. Mass Spectrom 217 (2002) 23.
[53] F.W. McLafferty, F. Tureček, Interpretation of Mass Spectra, 4th ed., University Science Books, Sausalito, CA, 1993.
[54] R.D. Bowen, P. Clifford, J.T. Francis, J.K. Terlouw, Int. J. Mass Spectrom. Ion Process. 165/166 (1997) 155.