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A mass spectrometric study of gasoline anti-knocking additives Part I: Electron impact ionization and fragmentation processes of MTBE

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Abstract

Methyl *tert*-butyl ether (MTBE) is the most widely used additive for gasoline as it is able to increase the oxygen content and to improve the efficiency in the internal combustion engine, controlling the autoignition.

Most of the experimental studies performed on MTBE give information only on neutral particle reaction schemes, preventing a complete understanding of the oxidation and pyrolisis reaction chemistry of MTBE in extreme conditions like for example those experienced in the reactions involved in a knocking engine during the spark ignition.

In the Part I of this work electron impact ionisation of MTBE has been studied in the range 25–150 eV by means of a time of flight mass spectrometry (TOF-MS). Total ionisation cross-section for MTBE and for all the ions formed from its fragmentation are evaluated relatively to Argon cross-section. What is learned by studying processes which can be understandable within a mass spectrometer can be applied to larger more applied systems, where the extreme conditions prevent an experimental study of the ion chemistry.

In the present study the MTBE cross-sections trends and the isotopic study of deuterated MTBE (MTBE-d_3) mass spectrum allowed to suggest reaction pathways for MTBE fragmentation.

This work will be extended to other two ether molecules, ETBE and TAME, that have been proposed in place of MTBE and the results will be described in the Part II of this paper.

Keywords: MTBE; Antiknocking; Gasoline; Mass spectrometry

1. Introduction

Abnormal combustion, more commonly known as knock or detonation, represents an important limit to the compression ratio at which an internal combustion engine can operate. As engine efficiency and fuel economy are approximately proportional to compression ratio under usual operating conditions, the occurrence of engine knock limits its performance. Suppression of knock can be achieved adding to the fuel octane-enhancing oxygenated organic compounds and aromatics instead of the undesiderable organolead compounds, but the effect of aromatics on toxic emissions make them less attractive and oxygenated compounds, such as alcohols or ethers, are preferentially used in reformulated gasolines [1,2].

The most widely ether used is the methyl *tert*-butyl ether (MTBE) that is able to increase the oxygen content and to improve the efficiency in the internal combustion engine, controlling the autoignition. The large use of MTBE in the last two decades brought about the high number of studies on the mechanisms of MTBE oxidation and pyrolisis in different operative conditions.

The chemical kinetic of the low-temperature oxidation of MTBE has been studied and modelled in detail in a static reactor at low pressures (200–100 Torr) and temperature (573–773 K)

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[3] and in similar temperature ranges (450–750 K) but in higher pressure conditions (7 bar, near to that occurring in the end gases of spark ignition engines) in a jet-stirred flow reactor [4]. High temperature oxidation of MTBE has been experimentally studied in a flow reactor [5] and in a shock tube [6,7] extending the kinetic model of Brocard et al. [3] to higher temperatures and pressures [7]. The autoignition of MTBE and other octane-enhancing ethers has also been examined in a motored-engine [8].

However, all these studies give information only on neutral particle reaction schemes, preventing a complete understanding of the oxidation and pyrolisis reaction chemistry of MTBE in extreme conditions like for example those experienced in the reactions involved in a knocking engine during the spark ignition.

The simulation of the spark ignition is often separated into two parts: breakdown phase and glow phase. During both the phases, but particularly during the breakdown phase of a spark ignition the concentration of ions relative to the neutral radicals is significant, and it is not adequate to include only the neutral particle reaction scheme in simulation work.

Ion reactions are in general much faster than the neutral particle reactions and, therefore, they should play more important roles at the early ignition stages until the high concentration of neutral radicals builds up and the thermal cracking dominates the combustion mechanism. High-energy ions are realistic at the very early stage of spark ignition; the temperature in the spark kernel can be well above 10,000 K [9] although the discharge volume at this stage is small and the gas rapidly relaxes to temperatures of few thousand K within microseconds.

Only some simulations, at least for the breakdown phase of the spark ignition, take in consideration the details of the electron and the ion kinetics including the ionisation cross-sections in the kinetic models [10].

In this contest, an electron impact ionization study versus electron energy for a largely used compound in motor engines like MTBE may provide useful data for the modelists. What is learned by studying processes which can be understandable within a mass spectrometer can be applied to larger more applied systems, where the extreme conditions prevent an experimental study of the ion chemistry.

In this work electron impact ionisation of MTBE has been studied in the range 25–150 eV by means of a time of flight mass spectrometry (TOF-MS). Total ionisation cross-section for MTBE and for all the ions formed from its fragmentation are evaluated relatively to argon ionisation cross-section.

The evaluation of the ionization cross-sections has been possible by the knowledge of the absolute ion yields as a function of electron energies measured from the kinetic energy distribution, as reported in a previous work [11].

In the present study the MTBE cross-sections trends and the isotopic study of deuterated MTBE (MTBE-d_3) mass spectrum allowed to suggest reaction pathways for MTBE fragmentation.

2. Experimental

The experimental apparatus has been described in detail in a previous paper [11] so that here we will summarize the principal features only.

The apparatus consists of vacuum chambers equipped with an effusive beam, an electron gun, and a linear time of flight mass spectrometer. The liquid sample (MTBE 99.8%; HPLC grade, Aldrich), behind the injector, was kept in a reservoir at a temperature of 28 °C in argon atmosphere.

The pressure in the reservoir, kept at 1.6×10^5 Pa, was stable within 0.1 Pa as measured by means of a Lesker fast response diaphragm manometer (range 15 to 2×10^{-2} Pa).

The temperature variation of the liquid, measured with a copper–constantan thermocouple, did not exceed 1 °C during all the measurement set. At this temperature the vapour pressure of the methyl *tert*-butyl ether is 3.3×10^4 Pa, as deduced from the Antoine coefficients, corresponding to 28% of the argon pressure in the reservoir.

The gas mixture interacts with the electron beam and the resulting ions are extracted from the source at 90° with respect to the nozzle axis and accelerated toward a multichannelplate (MCP) detector. The ion signals are acquired by means of a time-to-amplitude converter (TAC) and a multichannel analyser (MCA).

The mass spectra of all ionized fragments were recorded by varying the electron energy in the range 20–150 eV. We assume, based on the comparison with the argon ionization thresholds and in agreement with previous calibration of the apparatus, an accuracy of the measured electron energy of ±0.5 V [12].

Known the partial pressure of MTBE and Argon, the ion yield ratio of the fragments from MTBE and the Argon gives the fragment ionization cross-section relative to the Argon ionization cross-section by electron impact. The estimated error on the measurements presented here are within the 10% [11].

In order to have more insight on MTBE fragmentation an isotopic study has been performed. A comparison between MTBE and deuterated MTBE (MTBE-d_3, 99.8%; HPLC grade, Aldrich) fragmentation has been carried out at one value of energy (i.e., 70 eV). This has been accomplished by using a commercial quadrupole mass spectrometer allowing both an easier operation and the possibility of a quantitative analysis for a direct comparison of the ionic abundance of MTBE and MTBE-d_3 fragments.

The mass spectrometric apparatus utilized for MTBE-d_3 analysis is a gas chromatograph/Mass spectrometer. A Hewlett-Packard (HP), Model HP5890 GC is interfaced to an HP Model 5970 mass spectrometer equipped with an electron impact (EI) source and a quadrupole analyser. The ionising voltage is 70 eV. The source temperature is set at the factory to 250 °C. A known volume of the liquid sample was injected after vaporization in a syringe.

The same analysis in the same operative conditions was repeated on MTBE.

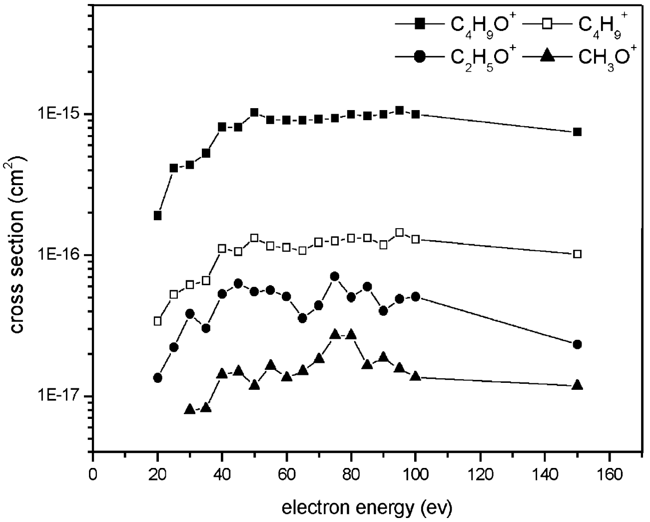


Fig. 1. Electron-impact ionization cross-section for the formation of CH_3O^+, $C_2H_5O^+$, $C_4H_9^+$ and $C_4H_9O^+$ ions from MTBE.

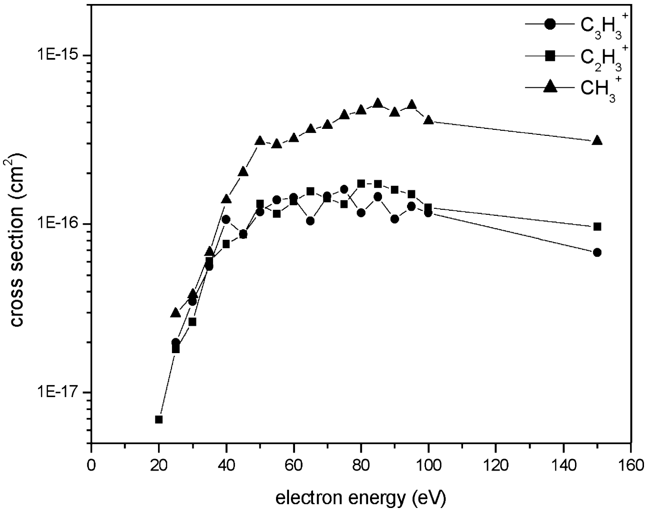


Fig. 3. Electron-impact ionization cross-section for the formation of CH_3^+, $C_2H_3^+$ and $C_3H_3^+$ ions from MTBE.

3. Results and discussion

In a previous work [11] total ionisation cross-section of MTBE and kinetic energy distributions of fragment ions over an energy range of 20–150 eV have been reported, as evaluated by taking into account the detection efficiency of the TOF mass spectrometer.

Cross-sections for the formation of various ions (not reported in the previous work) are shown in Figs. 1–4.

In Fig. 5a and b the mass spectra of MTBE [$(CH_3)_3OCH_3$)] and MTBE-d_3 [$(CH_3)_3OCD_3$] at 70 eV electron energy are reported (as obtained from the quadrupole mass spectrometer).

The sample pressure in the EI ion source is kept sufficiently low that bimolecular (“ion-molecule”) or other collision reactions are usually negligible, so that fragmentation process can be considered as unimolecular reactions. From energetic (20–150 eV) electrons the molecular ions are formed with a wide range of internal energies. If sufficiently excited, the M^+ ions can decompose by a variety of energy dependent reactions, each of them results in the formation of an ion or a neutral species; moreover, the primary ions may have sufficient energy to decompose further.

Generally, the main factor affecting the abundance of a product ion in a mass spectrum and therefore its formation pathway, is its stability. However, especially when more then one bond split and many rearrangements are involved, other information are necessary for establishing the reaction channel of each ion.

In the following paragraphs, considerations on ion stability have been matched with the comparison between the mass peaks from MTBE and MTBE-d_3 spectrum and the ionization cross-section trends versus energy in order to propose a reaction scheme for MTBE fragmentation.

Moreover, since the kinetic energy distributions (KEDs) of ions in the dissociative ionization is related to the fragmentation pathways, the KEDs of MTBE evaluated in a previous

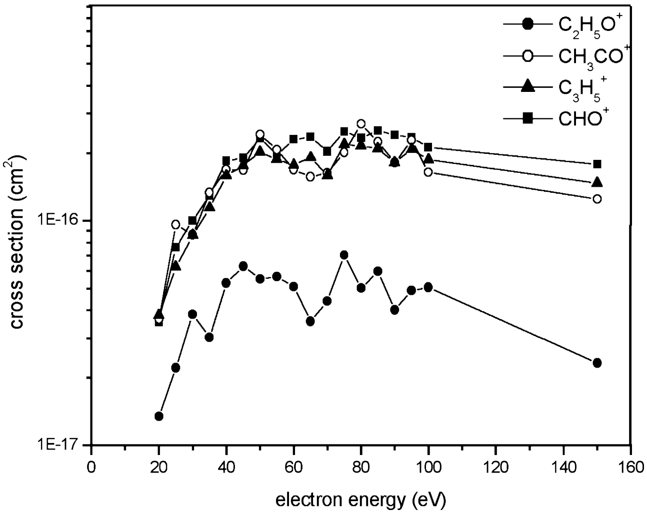


Fig. 2. Electron-impact ionization cross-section for the formation of CHO^+, $C_3H_5^+$, CH_3CO^+ and $C_2H_5O^+$ ions from MTBE.

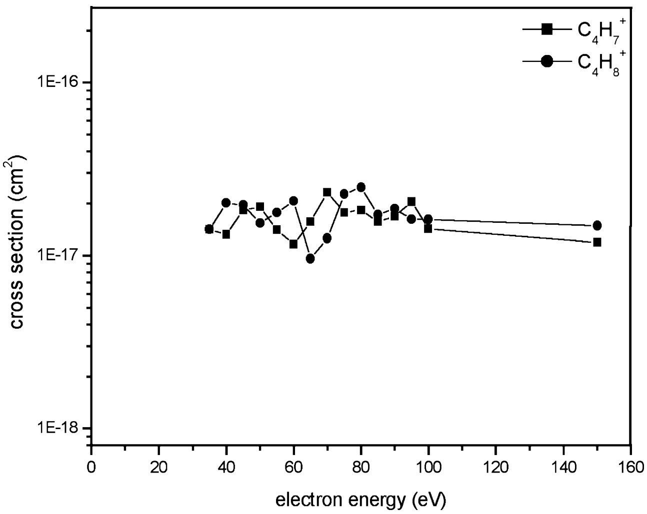


Fig. 4. Electron-impact ionization cross-section for the formation of $C_4H_7^+$ and $C_4H_8^+$ ions from MTBE.

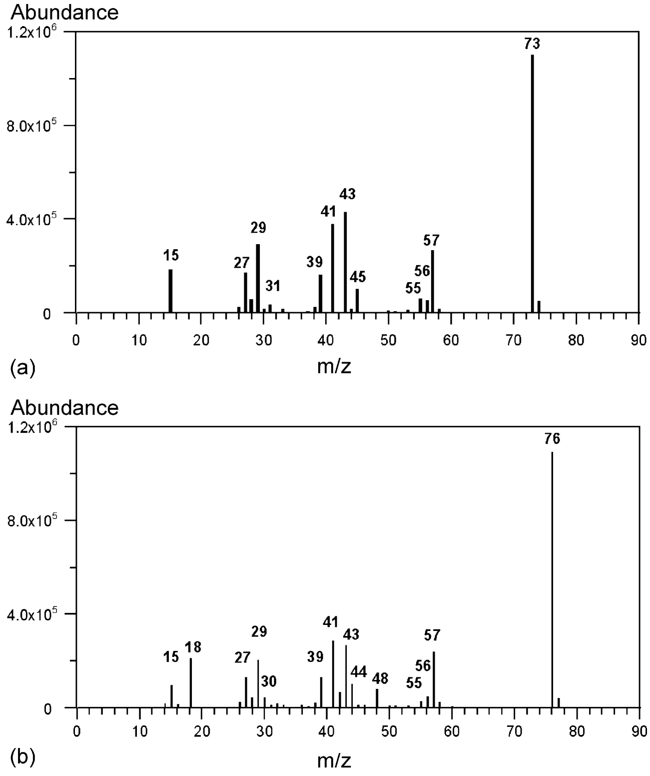


Fig. 5. Mass spectra of MTBE (a) and MTBE-d_3 (b) measured by quadrupole MS.

work [11] have been here analyzed for validating hypothesized fragmentation channels.

Considering the decomposition of a parent ion m$^+$ of mass m into two fragments of m_1 and m_2 masses:

$$m^+ \rightarrow m_1 + m_2{}^+$$

on the basis of conservation of energy and conservation of momentum laws, if E is the kinetic energy and $v = (2E/m)^{1/2}$ the velocity in a field-free region of a mass spectrometer, the following equations can be written:

$$E = E_1 + E_2$$

$$m_1 v_1 + m_2 v_2 = 0$$

and, using simple mathematic passages, it is possible to deduct that:

$$\frac{E_1}{E_2} = \frac{m_2}{m_1}$$

In order to apply this simple rule for the identification of a fragmentation pathway, it is necessary that the dissociation reaction forms only two fragments and that these fragments come only from that reaction. These conditions have never strictly verified for primary and secondary fragmentation reactions of MTBE. However, in some cases the similarity or the dissimilarity between kinetic energies of similar ion masses can give support or denial to a hypothesised pathway, as shown in the following.

3.1. Fragmentation paths

In Table 1 the relative intensities and electron impact ionisation cross-sections for the formation of selected ions with a cross-section greater than $1e - 17\ \mathrm{cm}^2$ at 70 eV are listed at three different electron energies: 20 eV, 70 eV (common voltage used in commercial MS) and 150 eV.

The mass spectrum is dominated over the whole range of ionisation energy by the base peak at $M/z = 73$ u.

The molecular ion peak, as expected from an aliphatic ether, tends to be from weak to negligible and it is visible only at high voltages [13], therefore it is not reported in the table.

Ionization of an aliphatic ether should occur preferentially by loss of an n-electron of the oxygen. Donation of the unpaired electron to the adjacent C–O bond is followed by transfer of an electron from another bond of this α-carbon atom [14]. The resulting one-electron bond then cleaves to give the alkyl radical and the resonance-stabilized oxonium ion; the greater the double-bond character of this ion, the lower will be the critical (activation) energy of the reaction. Note that only the radical site moves, the charge site remains on the oxygen.

In the case of MTBE the almost complete absence of the molecular ion peak suggests the large occurrence of a pri-

Table 1

Relative intensities and electron impact ionisation cross-sections for the formation of selected ions with a cross-section greater than $1e - 17\ \mathrm{cm}^2$ at 70 eV listed at three different electron energies: 20, 70 and 150 eV

Mass (u)	Ions	Relative intensity at 20 eV	σ (cm^2) at 20 eV	Relative intensity at 70 Ev	σ (cm^2) at 70 eV	Relative intensity at 150 eV	σ (cm^2) at 150 eV
73	$C_4H_9O^+$	100	1.89E−16	100	9.19E−16	100	7.43E−16
57	$C_4H_9{}^+$	17.97	3.40E−17	13.37	1.23E−16	13.68	1.02E−16
56	$C_4H_8{}^+$	0	0	1.37	1.26E−17	2.00	1.48E−17
55	$C_4H_7{}^+$	0	0	2.51	2.31E−17	1.60	1.19E−17
45	$C_2H_5O^+$	7.11	1.35E−17	4.78	4.39E−17	3.13	2.33E−17
43	CH_3CO^+	19.27	3.65E−17	17.72	1.63E−16	16.75	1.24E−16
41	$C_3H_5{}^+$	20.12	3.81E−17	17.28	1.59E−16	19.77	1.47E−16
39	$C_3H_3{}^+$	3.87	0	15.82	1.45E−16	9.13	6.78E−17
31	CH_3O^+	0	0	1.98	1.82E−17	1.59	1.18E−17
29	CHO^+	18.73	3.54E−17	22.12	2.03E−16	24.02	1.78E−16
27	$C_2H_3{}^+$	3.64	6.90E−18	15.37	1.41E−16	12.88	9.57E−17
15	$CH_3{}^+$	30.86	0	41.72	3.83E−16	41.44	3.08E−16

Table 2
List of the main ion masses from MTBE and MTBE-d_3 fragmentation (the percentage (%) in table indicates the relative amount of deuterated ion peak with respect to the undeuterated one)

Compound	M-15	M-31	M-32	M-33	M-43	M-45	M-47	M-49	M-59	M-61	M-73
MTBE	73	57	56	55	45	43	41	39	29	27	15
MTBE-d_3	76 (q[a])	57 (q)	56 (q)	55 (q)	48 (90%)	44 (40%) 46 (10%)	42 (12%)	39 (q)	30 (20%)	27 (q)	18 (60%)

[a] The symbol q denotes a quantitative transfer (>95%), after Djerassi et al., 1965 [15].

mary decomposition. From this primary decomposition the most abundant ions are formed (73 and 57 u).

The two most diagnostic processes of the aliphatic ethers upon electron bombardment are α-fission next to the oxygen atom and subsequent hydrogen transfer with ejection of an olefin molecule [15]. However, this last process did not occur with methyl ether, as this requires at least a β-hydrogen.

3.1.1. Formation of ions through a primary process

The primary decomposition of MTBE ($M/z = 88$ u) gives *t*-butyl oxonium ($M/z = 73$ u), methyl ion ($M/z = 15$ u), *t*-butyl ion ($M/z = 57$ u) and methyl oxonium ($M/z = 31$ u).

$C_4H_9O^+$ ($M/z = 73$ u) is the most abundant ion at all the voltage used (see Table 1) despite the high stability of $C_4H_9^+$ ($M/z = 57$ u and IE = 6.7eV). For justifying the formation of this oxonium ion from the α-fission next to the oxygen there is the rule of the “loss of the largest alkyl radical” [14]. For ethers there are six α-bonds. In the case of MTBE three of these are linked with methyl group and three with H, therefore the rule predicts the lost of CH_3 instead of an H. The three methyl groups are more or less equivalent so it is indifferent which of them is lost.

The chemical structure of *t*-butyl oxonium is also confirmed by the observation of Fig. 5b where the dominant peak is 76 u instead of 73. As the deuterium atoms are located in the methyl group linked to the oxygen, it means that the methyl group lost in the *t*-butyl oxonium formation is one of the three methyl group linked to the α carbon.

t-Butyl ion is formed from the cleavage of the C–O bond that gives the biggest alkyl ion. The other ion formed from this bond cleavage is the methyl oxonium, the smallest oxonium ion of the ether series $C_nH_{2n+1}O^+$ formed by alkyl groups lost (31, 45, 59, 73, ...) [14]. In fact in the MTBE-d_3 spectrum the ion 57 u has exactly the same abundance than in the MTBE spectrum, while the 31 u ion (methyl oxonium) is absent and 34 u ion (deuterated methyl oxonium) is present. Therefore the primary fission of C–O bond leaves all the deuterium atoms in methyl oxonium fragment.

The confirmation that $M/z = 73$, 57 and 31 u are formed through a primary process is also given by the ionisation cross-section trends reported in Fig. 1 and in Table 1 for three energy values.

The fact that the ion masses 73, 57 and 31 u present a threshold (40 eV) lower than all the other ions (50 eV), as observable in Figs. 1–4, indicates that their formation occurs early, i.e., directly from the molecular ion. Moreover, for the ion masses 73, 57 and 31 u the little variation of the cross-sections between 20 eV and the “plateau” value (only about twice, while for the other ions is from three to 10 times) suggests that these ions are not directly formed by electron collisions, but from molecular ions by means of a fast bond split [16].

As regard methyl ion, its trend is different from the other primary ion as it can be formed not only by a primary process but also by a lot of secondary processes.

This is confirmed also by the presence in the MTBE-d_3 spectrum of both 15 and 18 u ions.

3.1.2. Formation of ions through secondary processes

All the other ions from MTBE fragmentation are formed by secondary decomposition, i.e., from the daughter ions by C–C or C–O bond cleavage accompanied by atom rearrangement. In the following paragraphs the ions structure are proposed distinguishing between ions from *t*-butyl oxonium and ions from *t*-butyl ion.

This discrimination has been made mainly on the basis of a comparison between the deuterated and not deuterated spectrum of MTBE.

As the *t*-butyl oxonium is completely deuterated and *t*-butyl cation does not contain any deuterium atom it can be reasonable to assume that ions appearing with lower abundance in MTBE-d_3 spectrum with respect to MTBE one are formed as a preferential channel from *t*-butyl oxonium and ions appearing unchanged in the two spectra are formed from *t*-butyl cation.

In Table 2 the list of the main ion masses from MTBE and MTBE-d_3 fragmentation has been summarized for comparison.

The formation channels of the secondary ions are proposed in the following paragraphs by matching the observation of Fig. 5a and b and Table 2 with the reaction paths requiring the minimum number of bond cleavage and atom rearrangement and the cross-section trend versus impact electron energy.

Ions from *t*-butyl oxonium:

$M/z = 45$ u

Ethyl oxonium $C_2H_5O^+$ could be the species with $M/z = 45$ u as it is a very stable ion and it is the second species (two C atoms) from the ether series $C_nH_{2n+1}O^+$, therefore its formation is expected from ether fragmentation [14].

In this hypothesis, the ethyl oxonium could be formed from the fragmentation of *t*-butyl oxonium by means of a C–O and a C–C cleavage followed by CH_3 and H rearrangements.

In Fig. 2 the ionization cross-section trend of the three species from the ether series ($C_4H_9O^+$, $M/z = 73$, $C_2H_5O^+$, $M/z = 45$ and CH_3O^+ $M/z = 31$) are contrasted in the same graph, showing their similarity and also the progressive decreasing of intensity with the decrease of carbon atom number.

Table 3
Values of the thermal energy of the fragment ions, measured at 70 eV electron energy

Mass (u)	73	57	56	55	45	43	41	39	31	29	27	15
E_{th} (eV)	0.065	0.027	0.037	0.044	0.1	0.143	0.08	0.12	0.073	0.071	0.14	0.16

In the MTBE-d_3 spectrum (Fig. 5b) the 45 u ion is almost completely absent whereas the ion with $M/z = 48$ u (CD_3CHOH+) has an abundance (90%, Table 2) comparable with the 45 u ion in the MTBE spectrum. This supports its formation from *t*-butyl oxonium and validates the main occurrence of the pathway proposed.

$M/z = 43$ u, 41, and 29 u

The fragment ions with masses 43 and 29 u could belong to the alkyl series $C_nH_{2n+1}{}^+$ or to ketonic $C_{n-1}H_{2n-1}O^+$ series that are overlapped since CO and C_2H_4 are not resolved in mass. When more than one bond is broken only considerations on product stability are not enough to assess the fragmentation process. By contrast the isotopic study can help in this discrimination.

The fragmentation of *t*-butyl oxonium can lead, trough C–C and O–C bond splits, to the acetyl cation with $M/z = 43$ u (CH_3CO^+), whose stability is due to the electron sharing involving a non bonding orbital of oxygen atom. The main occurrence of this path for 43 u ion formation is supported by the reduction of more that 50% of its signal in MTBE-d_3 spectrum with respect to the MTBE spectrum (Table 2) and by the appearance of two ions with $M/z = 44$ and 46 u. These masses can correspond to acetyl cation with one and three deuterium atoms, respectively, suggesting the occurrence of some H rearrangements after the two bonds split.

In Fig. 2 the ionization cross-section trend versus energy of the ion 43 u is reported along with those of 45, 41 and 29 u. The curves for 43, 41 and 29 u ions are almost completely coincident, both in intensity and in trend, suggesting a similarity in the reaction channels of their formation.

However, in the case of 41 u ions, it is hard to hypothesize an oxygenated structure as the only specie corresponding to this mass can be the chetene ion (CH^+CO), extremely instable. More plausible is to attribute the very stable structure of allyl cation ($CH_2CHCH_2{}^+$) to 41 u ion, which can be formed from *t*-butyl oxonium by C=O bond split followed by H rearrangements leadings to the mass 42 u in MTBE-d_3, due to the presence of a deuterium atom. However, the comparison between deuterated and not deuterated spectrum of MTBE reveals a lowering of just 12% of 41 u ion peak (Table 2), suggesting the occurrence of two competitive reaction channels for its formation: one, already described before, from *t*-butyl oxonium, and the latter, more important, described in the following paragraph, from *t*-butyl cation.

The structure hypothesized for 29 u ion is acyl ion (CHO^+) due to the stability of this ion and even if the reduction of its abundance is only about 20% in the MTBE-d_3 spectrum with the corresponding formation of the 30 u ion. This reduction of not deuterated ion along with the ionization cross-section trend of Fig. 2 supports, although not in definitive way, the main path formation of the 29 u ion from *t*-butyl ether by two C–C and one C–O bond split with hydrogen rearrangement leading to about 20% of deuterated acyl cation (CDO^+).

Using the equation obtained before from energy and momentum conservation laws:

$$\frac{E_1}{E_2} = \frac{m_2}{m_1}$$

and the KEDs values calculated at different electron energy (reported only at 150 eV) in a previous work [11] and reported in Table 3 at 70 eV, it is possible to validate the path formation of 29 u ion from *t*-butyl ether by two C–C and one C–O bond split described before.

Indeed, the energies reported in Table 3 for 29 and 27 u ion masses are very different ($E(27)$ about twice $E(29)$) even if their masses are almost equals to and therefore it is possible to exclude their provenience from the same reaction channel with the only difference of a further loss of two hydrogens in the case of the 27 ion. As the formation of 27 u ion from *t*-butyl cation fragmentation is well assessed, as described in a following paragraph, the provenience of the 29 u ion from the same cation is not probable.

In the same way, the comparison between 43 and 41 u energies from Table 3 reveals that they are not coming from the same fragmentation path. In fact, a further loss of two hydrogens from the 45 u ion should cause an increase of energy while the energy of the 41 u ion is only about 60% of the energy of the 43 u ion, confirming the different structures attributed to them in the previous discussion.

Ions from *t*-butyl cation:

$M/z = 56$ u

The split of just one C–H bond lead to the formation of isobutene ($C_4H_8{}^+$).

The formation of isobutene in mass spectrometric conditions has to be underlined as it is the main product of MTBE decomposition in spark-ignited engines.

The most important feature of isobutene is the fact that it has six allylic H atoms, which are more easily abstracted than conventional primary H atoms. The 2-methyl allyl radical which is then produced is relatively unreactive and its β-scission products, allene and methyl radical, are extremely unreactive. This explains the antiknocking effect of MTBE addition to gasoline.

$M/z = 55$, 41, and 27 u

The ions with masses 55, 41, and 27 u can be peaks from the alkenyl serie C_nH_{2n-1} so corresponding to isobutyl cation ($C_4H_7{}^+$), allyl cation ($C_3H_5{}^+$) and vinyl cation ($C_2H_3{}^+$), respectively. As regard the 55 and 27 u ions, their structure and their reaction channels from fragmentation of *t*-butyl cation are suggested by their high stability and by their unchanged abundance in the MTBE-d_3 spectrum (see Table 2). Isobutyl cation can be formed by just two C–H bond split, with the formation of a double delocalized C=C bond that gives stability to the molecule. Vinyl cation can be formed by two C–C bond and one C–H bond split, with the formation also in this case of a double C=C bond.

As discussed in the previous paragraph, for the 41 u the most plausible structure is the allyl cation, but the reduction of about 10% of its abundance in the MTBE-d_3 spectrum suggests the occurrence of two competitive reaction channels, with a preference for the channel from *t*-butyl cation. In this case just one C–C and two C–H bond splits are required.

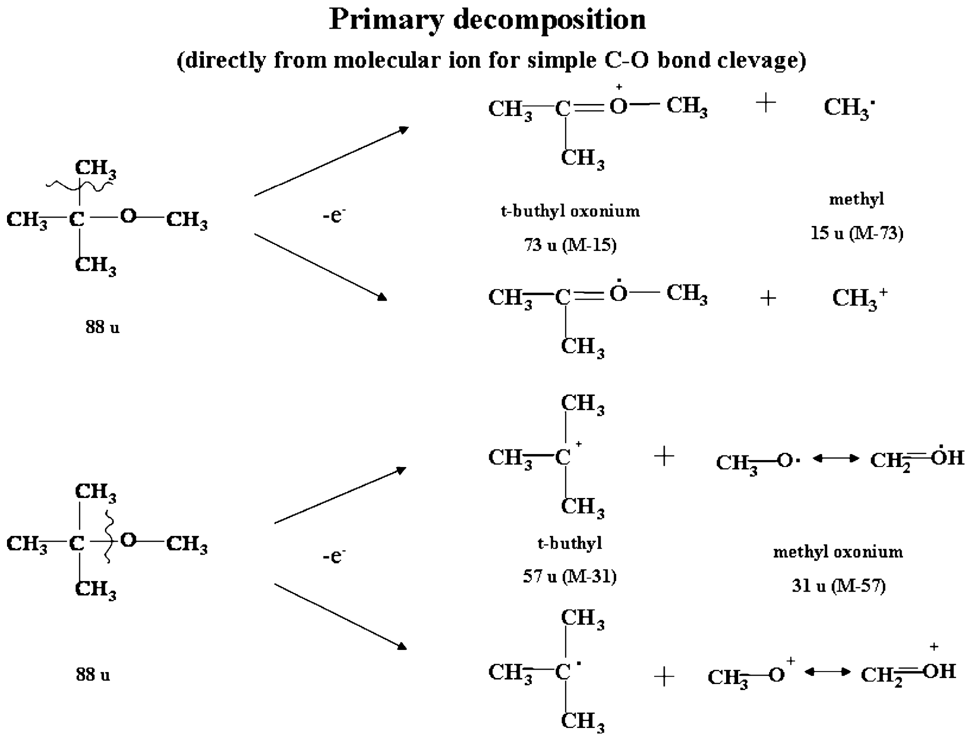
The structure attributed to 39 u ion is that of the propargyl cation ($C_3H_3^+$) and its exclusive formation path is from *t*-butyl cation fragmentation, as testified by the absence of any deuterated homologus (Table 2). The fragmentation occurs trough one C–C bond split and three C–H bond splits and the formation in the produced ion of two double C=C bonds whose delocalization gives great stability to the ion.

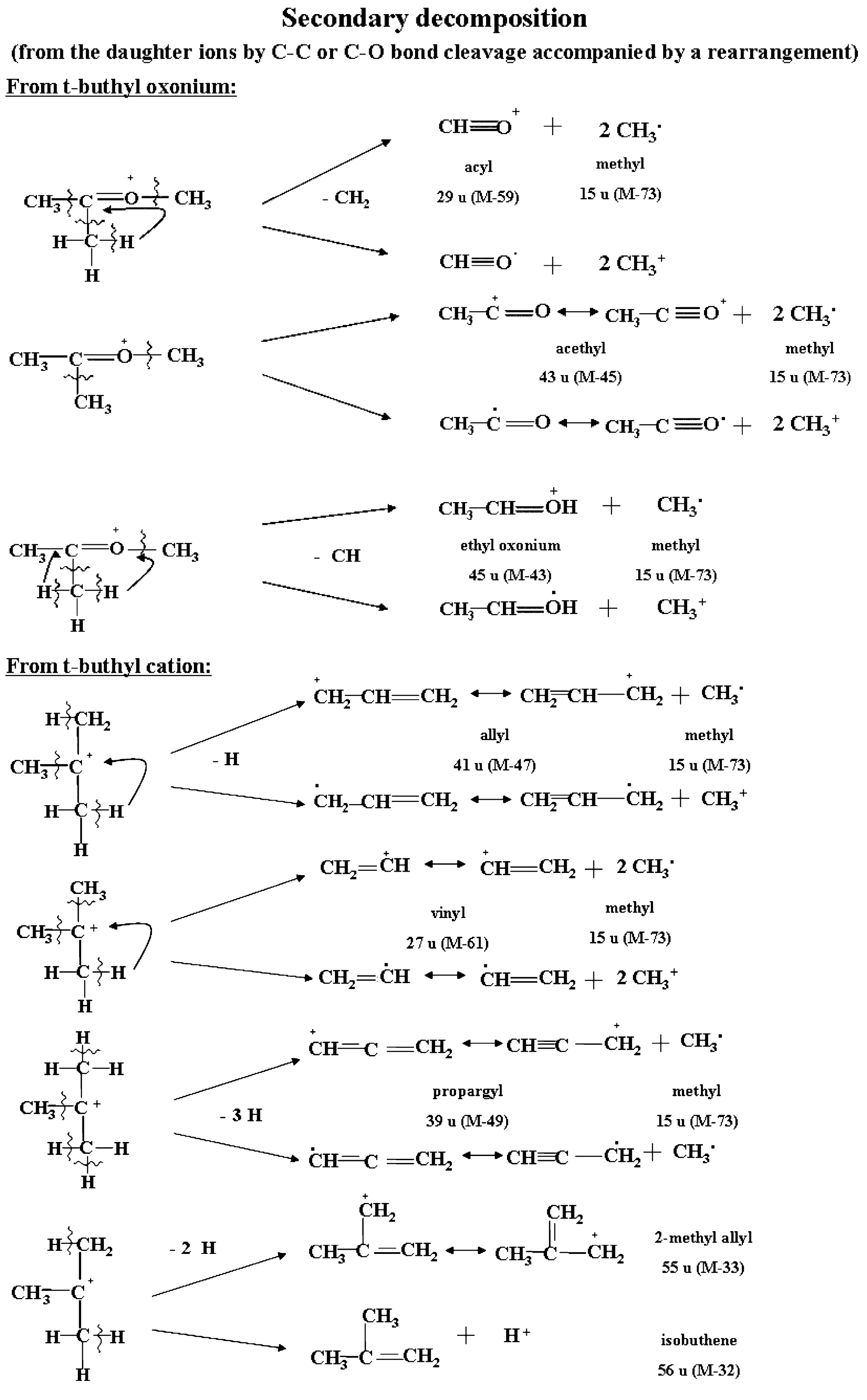
4. Conclusions

In this work electron impact ionization of MTBE has been studied in the range 20–150 eV by means of a time of flight mass spectrometry (TOF-MS). Total ionization cross-section for MTBE and for all the ions formed from its fragmentation are evaluated relatively to argon cross-section.

The MTBE cross-section trends along with the isotopic study of deuterated MTBE (MTBE-d_3) mass spectrum allowed suggesting reaction pathways for MTBE fragmentation, as summarized in the following schemes:

5. Summary of the proposed reaction scheme for the MTBE fragmentation





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