



## Isomeric effects on fragmentations of crotonaldehyde and methacrolein in low-energy electron–molecule collisions

Arup Kumar Ghosh, Aparajeo Chattopadhyay, Anamika Mukhopadhyay, Tapas Chakraborty\*

Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700032, India

### ARTICLE INFO

#### Article history:

Received 19 December 2012

In final form 18 January 2013

Available online 26 January 2013

### ABSTRACT

Fragmentation behavior upon low energy (10–16 eV) electron molecule collision of two isomeric  $\alpha,\beta$ -enones, crotonaldehyde and methacrolein, has been studied by quadrupole mass spectrometry. Three predominant reaction channels identified immediately above the ionization threshold are H, CO and HCO losses from the parent molecular ions, and isomeric effects are vividly manifested with respect to these channels. Signals corresponding to  $\text{CH}_3\text{C}=\text{O}^+$  ion, produced due to methyl migration, are displayed only by methacrolein. The observed isomeric effects are interpreted using the energies of the transition states and thermodynamic stabilities of the products predicted by calculation at DFT/B3LYP/6311++G(d,p) level.

© 2013 Elsevier B.V. All rights reserved.

### 1. Introduction

Low kinetic energy (KE) electrons can induce various chemical events when allowed to interact with molecules of different sizes and complexities [1,2]. Electrons of KE as low as 0.8 eV are known to break the DNA strands [3]. The origin of this chemistry is suggested as due to attachment of such electrons onto the  $\pi^*$  valence molecular orbitals of DNA bases. Bond cleavage and rearrangement reaction of relatively smaller molecules have also been observed with low KE electrons, e.g., the case of various aliphatic alcohols, amines, carboxylic acids, fluoroalkanes and even DNA bases [4,5]. For electron energies less than 4 eV hydrogen abstraction channel has been found to be dominant reaction channel in each case. Within 4–10 eV of electron kinetic energy (e-KE) range, other channels open up but  $\text{H}^-$  ion formation channel is still significant due to core excited resonances located on different sites of the molecules. For example, the  $\text{H}^-$  channel of methanol displays three resonances at 6.4, 7.9 and 10.2 eV, and of these the first two have been assigned to be located at the O–H site. The last one, which has been assigned to be located at the C site, is a characteristic of alkanes. For most of the carbonyl compounds the first ionization energies fall in the energy range 9.5–11 eV. Immediately above the ionization thresholds, these molecules undergo are known to important structural rearrangements such as McLafferty rearrangement [6].

Photochemical reactions in the gas phase of volatile organic compounds (VOCs) induced by electrons and/or by solar UV radiation are very important to understand the details of their atmospheric implications [7]. In this Letter we report the

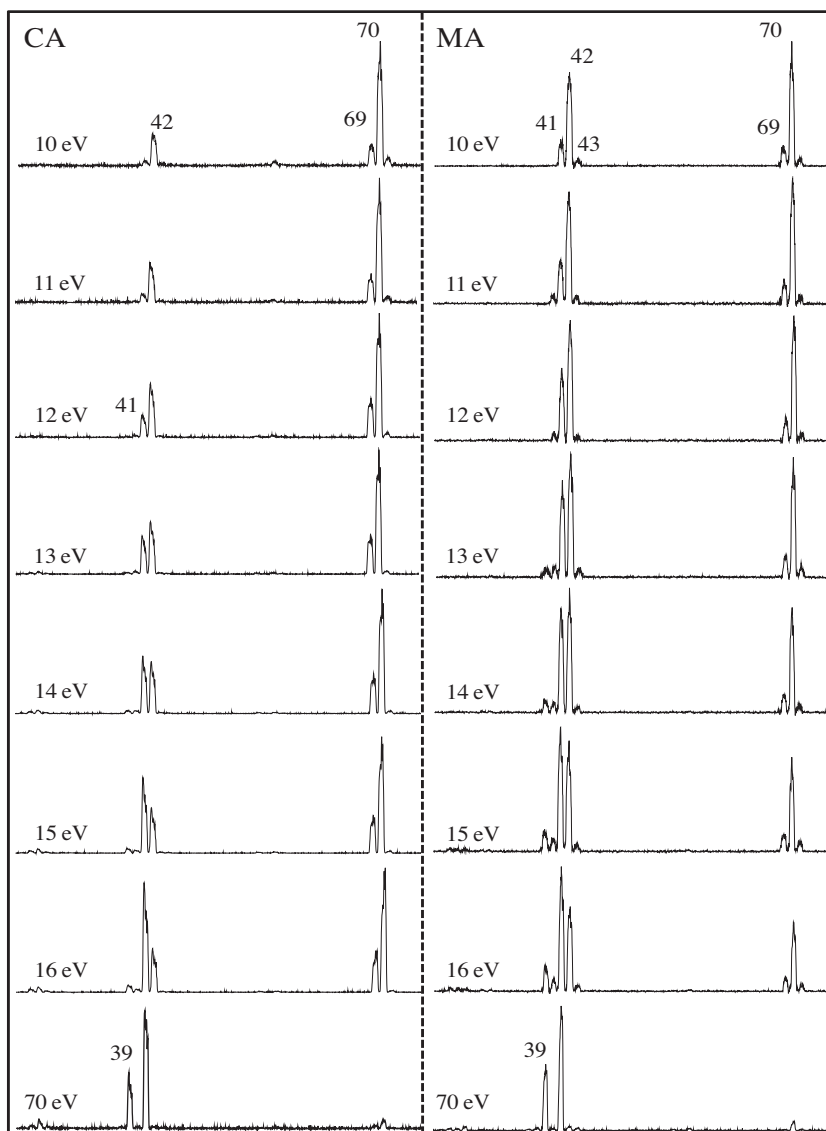
fragmentation behavior of two isomeric  $\alpha,\beta$ -enones, crotonaldehyde (CA) and methacrolein (MA) upon electron molecule collisions of electron energy immediately above their ionization thresholds for the first time. CA is released into atmosphere as direct biological emission and partial oxidation of fuels and other VOCs [8–10], and MA is produced primarily as the oxidation product of isoprene in our atmosphere [11–13].

The ionization energy of CA has been measured to be  $9.73 \pm 0.01$  eV using photoionization study by Watanabe et al., where  $\text{H}_2$  emission lines were used as light source for ionization [14]. The same has been reported to be  $9.86 \pm 0.03$  eV using ultraviolet photoelectron spectroscopy by Klessinger et al. [15]. Thus, although MA is isomeric to CA, the ionization energy of the former is  $\sim 0.15$  eV higher [16]. In this connection, the study of fragmentation pattern of the molecular ions generated with limited internal energy is expected to provide valuable information about the dynamics of the energized molecules that result to chemical events. Several studies were devoted in the recent past on electronic spectroscopy and UV photochemistry of these molecules in the gas phase [17–31]. However, to our knowledge, the chemical outcome following low energy electron–molecule collisions of these systems are not known.

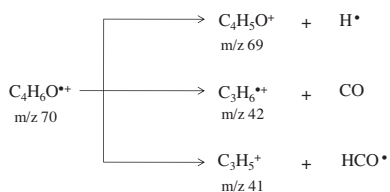
In the ground state, both the molecules can exist over two conformational forms, s-trans and s-cis. In the case of CA, the s-trans form has been found to be present predominantly (>98%) [32,33], and the calculated difference in energy between the two conformers of CA is 2.5 kcal/mol [32]. The first electronic absorption band for  $S_1 \leftarrow S_0$  transition of the molecule appears within 250–400 nm range in the vapor phase. The origin region of this spectrum shows several vibronic structures. The second transition ( $S_2 \leftarrow S_0$ ) appears within 190–250 nm range with a maximum at about 203 nm [17–19]. Photolysis in the vapor phase results in

\* Corresponding author. Fax: +91 3324732805.

E-mail address: [pctc@iacs.res.in](mailto:pctc@iacs.res.in) (T. Chakraborty).



**Figure 1.** Ionic fragments produced by electron–molecule collisions at different e-KE probed by quadrupole mass spectrometry.



**Figure 2.** Fragmentation channels corresponding to formation of  $m/z$  69, 42 and 41 ions arising from CA and MA.

CO and propylene as the major products along with small amounts of  $\text{C}_2\text{H}_4$ ,  $\text{H}_2$ ,  $\text{CH}_4$ , allene, propyne and cyclopropane [30,31]. The molecule also undergoes photoisomerisation upon excitation within 245–400 nm range to produce 3-buten-1-al, ethylketene (EK) and the enol form of CA [31]. In inert argon matrix, photo-isomerization resulting in formation of the isomeric *s-cis* conformer is the major outcome of UV excitation [34]. It has been suggested that small amounts of CO and EK are also formed under such conditions. Such conformational isomerisation in the cold matrix has also been observed for MA [34]. Shu et al. have used photofrag-

ment translation spectroscopy (PTS) to investigate the 193 nm (ArF excimer laser) photodissociation of CA and identified three dissociation channels corresponding to loss of H atom, methyl group and CO [35]. It has been suggested that H loss occurs in the ground state potential energy surface, while the CO loss takes place following isomerisation of CA into EK. The occurrence of a fourth reaction channel corresponding to HCO and/or  $\text{C}_2\text{H}_5$  loss is also suggested. In contrast, vapor phase photolysis or photochemistry of MA is less known. From the viewpoint of atmospheric importance, only the reaction of this molecule with OH radical has been studied, experimentally as well as theoretically [36,37]. In the following sections, the observed fragmentation behaviors of CA and MA upon interaction with low energy electrons are presented, and these are analyzed with the aid of the prediction of electronic structure calculation.

## 2. Experiment

The experimental set up has been described elsewhere [38,39]. Briefly, the sample vapor was introduced in the ionization region via an effusive nozzle of diameter 100  $\mu\text{m}$  and a working pressure

Download English Version:

<https://daneshyari.com/en/article/5382163>

Download Persian Version:

<https://daneshyari.com/article/5382163>

[Daneshyari.com](https://daneshyari.com)