

# Absolute electron impact ionization cross-sections and polarizability volumes for the C<sub>2</sub> to C<sub>6</sub> methanoates and C<sub>3</sub> to C<sub>7</sub> ethanoates

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## Abstract

Absolute total positive ion electron impact ionization cross-sections from 15 to 285 eV are reported for the C<sub>2</sub> to C<sub>6</sub> methanoates (formates) and the C<sub>3</sub> to C<sub>7</sub> ethanoates (acetates), including all isomers. The reproducibility of the measured cross-sections over the full energy range is better than ±4%, and absolute cross-sections measured for a series of reference species (N<sub>2</sub> and inert gases) are in excellent agreement with values reported by several other groups claiming accuracies of around ±5%. A monotonic relationship is shown to exist between the maximum ionization cross-sections for the esters, reported here, the C<sub>1</sub> to C<sub>4</sub> alcohols, reported previously, and the total number of carbon atoms in the skeletal chain. The relationship provides a useful means for estimating unknown cross-sections. Polarizability volumes for esters may be estimated using a previously established correlation with the maximum ionization cross-section, and for the four species for which published data are available the predictions are in good agreement with experiment. Finally, the experimental data are compared with calculations carried out using the binary encounter Bethe (BEB) method for the calculation of total ionization cross-sections.

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**Keywords:** Ionization cross-section; Electron impact ionization; Polarizability volume; Ionization of esters

## 1. Introduction

The influence of functional group, molecular shape and size, molecular orientation and three-dimensional structure on ionization efficiency has revealed some interesting and useful correlations between the maximum electron impact ionization cross-section and other fundamental molecular parameters, such as molecular polarizability volumes and ionization potential [1–9]. Accurate measurements of the absolute total ionization cross-section may be used together with empirical and theoretical relationships to estimate unknown values for other molecular parameters, such as molecular polarizability volume, and may also be used to test theoretical predictions [10,11]. Electron impact ionization plays an important role in many areas of chemistry and physics, including mass spectrometry, plasma

processes and gas discharges. Accurate ionization cross-sections are important for understanding the mechanism of the ionization process, and they are also required for modelling applications ranging from studies of fusion plasma degradation to investigations into radiation effects in medicine and materials science.

In the present work, we report absolute total electron impact ionization cross-sections for the C<sub>2</sub> to C<sub>6</sub> methanoates (formates) and the C<sub>3</sub> to C<sub>7</sub> ethanoates (acetates), including all isomers, from a few eV above threshold to 285 eV. Experimental values for the maximum ionization cross-section are compared with values calculated using the Binary Encounter Bethe method of Kim and Rudd [12–16].

## 2. Experimental

The ionization cell used for these measurements has been described previously [4,17]. The ionization cell is housed in a vacuum chamber with a typical background pressure of ~10<sup>-7</sup> Torr. Permanent rare-earth magnets with nominal pole strength of 6000 G are used to collimate the electrons emitted from a resistively heated rhenium filament, which is biased at

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a potential that determines the electron energy. The effect of the magnetic field on electron path length is small but has been taken into account [4]. The walls of the heated brass ionization cell are coated with colloidal graphite in order to prevent surface scattering of charged particles, an important consideration since the cell walls also serve as the ion collector. The trap current is regulated to a preset value in the range from 75 to 100 nA using feedback control of the filament current. Since the electron energy distribution exhibits a FWHM of around 1 eV, and the trap current regulation becomes unstable below 15 eV, we have not attempted to report ionization thresholds (appearance energies). However, the cross-section for the ionization of N<sub>2</sub> in the region of the ionization threshold is measured using a non-regulated filament current supply in order to estimate the effect of contact potentials on the electron energy scale and this has been reported previously [17].

Analar grade (>99.0%) methyl ethanoate, ethyl ethanoate, *n*-propyl ethanoate, *n*-butyl ethanoate and *n*-amyl ethanoate from Aldrich were dried over MgSO<sub>4</sub> and further purified by fractional distillation under atmospheric pressure. *iso*-Propyl ethanoate, *iso*-butyl ethanoate, *sec*-butyl ethanoate, *tert*-butyl ethanoate were synthesized as follows: to a stirred and gently refluxed solution of the corresponding alcohol (77 mmol, approximately 7.3 mL) and *N,N*-dimethylaniline (10.6 mL, 84 mmol) in anhydrous ether (10 mL), analar acetyl chloride (5.6 mL, 79 mmol) was added dropwise over a period of 30 min with stirring for a further 60 min at the same temperature. The base *N,N*-dimethylaniline was added in order to increase the reaction rate and to prevent acid-catalysed side reactions such as dehydration or alkyl halide formation with tertiary alcohols [18]. The resultant mixture was allowed to cool to room temperature, distilled H<sub>2</sub>O added (10 mL) and stirring recommenced until all the precipitated *N,N*-dimethylaniline hydrochloride had dissolved. The top organic phase was separated and washed with cold 10% H<sub>2</sub>SO<sub>4</sub> (3 × 3 mL), dried over MgSO<sub>4</sub> overnight and purified by fractional distillation under atmospheric pressure.

<sup>1</sup>H NMR spectra of all samples were recorded on a 500 MHz Oxford AS 500 spectrometer using CDCl<sub>3</sub> as an internal reference. Both <sup>1</sup>H NMR spectroscopic data and the boiling points measured during fractional distillation were in accord with those reported in Aldrich [19] for samples of 99% or greater purity, indicating high purity of the prepared samples.

Absolute electron ionization cross-sections,  $\sigma_i$ , are calculated from Eq. (1):

$$\frac{I^+}{I^-} = n\sigma_i x \quad (1)$$

where  $I^+$  and  $I^-$  are the measured ion and electron currents,  $n$  the number density of the target gas and  $x$  is the path length through the collision cell. Assuming ideal gas behaviour, the above expression can be rewritten as:

$$\frac{I^+}{I^-} = \frac{P\sigma_i x}{k_B T} \quad (2)$$

where  $P$  and  $T$  are the pressure and temperature of the target gas and  $k_B$  is Boltzmann's constant.

Ionization efficiency curves are highly reproducible from run to run, even for experiments carried out several weeks apart. The results reported here are the averages of between 5 and 10 repeated determinations for each target gas, made over a period of several months. Before and after each data run, three to five measurements were made of the ionization efficiency curve for N<sub>2</sub>. These were compared with the data recommended in the compilation by Lindsay and Mangan [9] as an independent assessment of the accuracy of the data. The recommended maximum cross-section for N<sub>2</sub> is given as 2.51 Å<sup>2</sup> (±5%) and the absolute values measured in this work always fall within the range 2.50–2.52 Å<sup>2</sup>.

### 3. Results and discussion

Cross-section data for the C<sub>2</sub> to C<sub>6</sub> methanoates (formates) and the C<sub>3</sub> to C<sub>7</sub> ethanoates (acetates) are shown graphically in Figs. 1 and 2. Tabulated data can be obtained from the corresponding author on request. A plot of the maximum ionization cross-section,  $\sigma_{\max}$ , for the methanoates, ethanoates and the C<sub>1</sub> to C<sub>4</sub> alcohols, reported previously, as a function of the number of carbon atoms,  $n_C$ , in the molecule is shown in Fig. 3. The component of cross-section for the addition of each –CH<sub>2</sub> unit is shown to be 2.67 Å<sup>2</sup>, Eq. (3):

$$\sigma_{\max} = 2.67n_C + 2.34 \quad (3)$$

where the goodness of fit  $R^2 = 0.997$ . Since this plot includes the methanoates, ethanoates and alcohols [17], Eq. (3) could be used

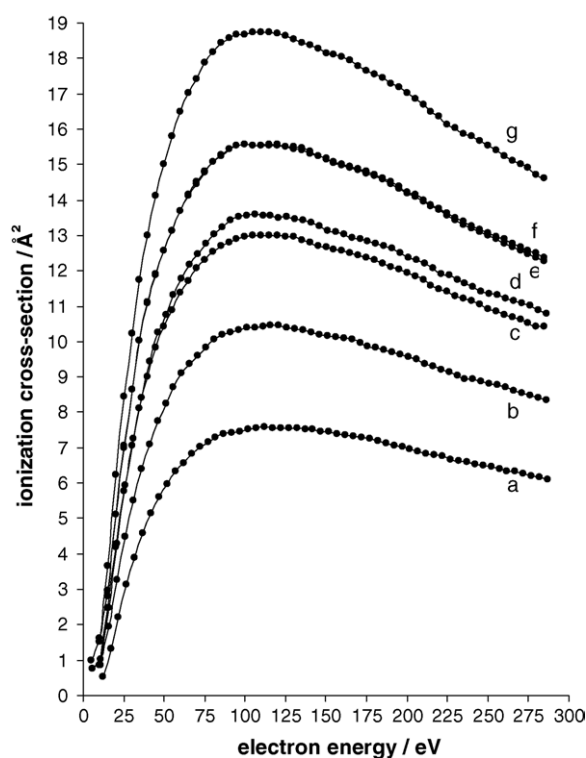


Fig. 1. Ionization cross-section vs. electron energy for the methanoates: a, methyl methanoate; b, ethyl methanoate; c, *iso*-propyl methanoate; d, *normal*-propyl methanoate; e, *iso*-butyl methanoate; f, *normal*-butyl methanoate; g, *normal*-amyl methanoate.

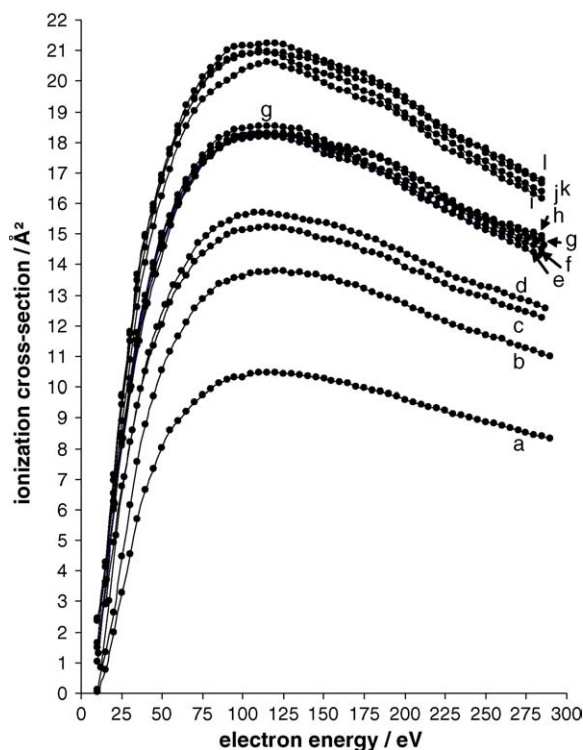


Fig. 2. Ionization cross-section vs. electron energy for the ethanoates: a, methyl ethanoate; b, ethyl ethanoate; c, *iso*-propyl ethanoate; d, *normal*-propyl ethanoate; e, *secondary*-butyl ethanoate; f, *normal*-butyl ethanoate; g, *tertiary*-butyl ethanoate; h, *iso*-butyl ethanoate; i, *iso*-amyl ethanoate; j, *normal*-amyl ethanoate; k, *tertiary*-amyl ethanoate; l, *secondary*-amyl ethanoate.

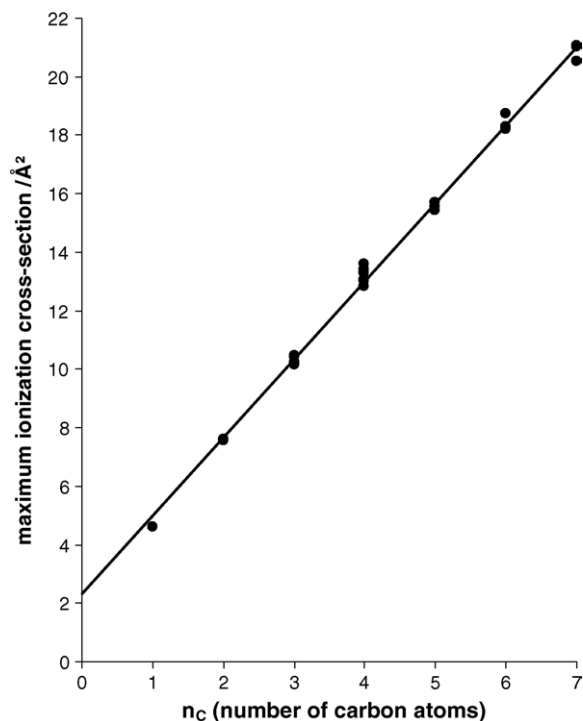


Fig. 3. Plot of the maximum ionization cross-section vs. the number of skeletal carbon atoms for the C<sub>1</sub> to C<sub>4</sub> alcohols, the C<sub>2</sub> to C<sub>6</sub> methanoates and the C<sub>3</sub> to C<sub>7</sub> ethanoates. The best line fit to the data is given by Eq. (3).

to estimate maximum ionization cross-sections for alcohols with higher molar mass or for esters based on higher organic acids, such as the propanoates. The variation in  $\sigma_{\max}$  for the isomeric forms of the esters cannot be considered to be significant in terms of the  $\pm 5\%$  accuracy claimed on these measurements.

We have previously reported on relationships between the maximum total electron impact ionization cross-section and molecular electrostatic parameters. It has been shown from first principles [10,11] and confirmed experimentally [20] that linear relationships exist between the maximum cross-section  $\sigma_{\max}$  and the molecular polarizability volume  $\alpha$ , Eq. (4), and with the quantity  $(\alpha/E_0)^{1/2}$ , Eq. (5), in which  $E_0$  is the ionization potential for production of the molecular ion:

$$\sigma_{\max} = c''\alpha \quad (4)$$

$$\sigma_{\max} = c' \left( \frac{\alpha}{E_0} \right)^{1/2} \quad (5)$$

In these expressions,  $c'$  and  $c''$  are empirically determined constants. Polarizability volumes are used in the calculation of a range of physical parameters, including: modelling of refraction by polar and non-polar molecules; the calculation of dielectric constants and diamagnetic susceptibility; ion mobility in gases; long-range electron–molecule and ion–molecule interaction energies; Langevin capture cross-sections and rate constants for polar and non-polar molecules; van der Waals constants; and oscillator strengths. A plot of  $\sigma_{\max}$  in  $\text{\AA}^2$  versus  $\alpha$  in  $\text{\AA}^3$  for 68 atoms and molecules from He to C<sub>10</sub>H<sub>22</sub>, including small molecules such as H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, NH<sub>3</sub>, hydrocarbons, per-fluorocarbons, chlorocarbons, nitriles, mixed halocarbons and alcohols, is shown in Fig. 4. Intersection points for measured maximum ionization cross-sections and the literature values for the published polarizability volumes for the methyl and ethyl methanoates and ethanoates [21–23] are shown as open circles in the figure. The best fit to the points, excluding the esters, gives:

$$\sigma_{\max} = 1.400\alpha \quad (6)$$

where  $R^2 = 0.952$ . The main contribution to the scatter in this plot is the range in values of published polarizability volumes for many of the molecules for which ionization cross-sections have been measured, in particular the halocarbons, for example ( $\text{\AA}^3$ ), 5.72 [24] and 5.59 [25] for CFC<sub>3</sub>, 11.2 [25] and 10.5 [26] for CCl<sub>4</sub>, 9.5 [27] and 8.23 [22] for CHCl<sub>3</sub>, 9.32 [25] and 8.62 [23] for CH<sub>2</sub>Br<sub>2</sub>, 6.48 [26] and 7.93 [25] for CH<sub>2</sub>Cl<sub>2</sub>, 6.03 [25], 5.87 [24], and 5.55 [28] for CH<sub>3</sub>Br and 5.35 [24] and 4.72 [27] for CH<sub>3</sub>Cl. The correlation between maximum ionization cross-section and polarizability volume described by Eq. (6) offers an alternative route to the estimation of unknown polarizability volumes.

Measured maximum ionization cross-sections and values calculated using the BEB method are shown in Table 1 and Fig. 5. A best line fit to the data gives:

$$\sigma_{\max}(\text{BEB}) = 0.91\sigma_{\max}(\text{experimental}) \quad (7)$$

where  $R^2 = 0.991$ . Although this represents a 10% difference between experiment and theory, the origin of the discrepancy is

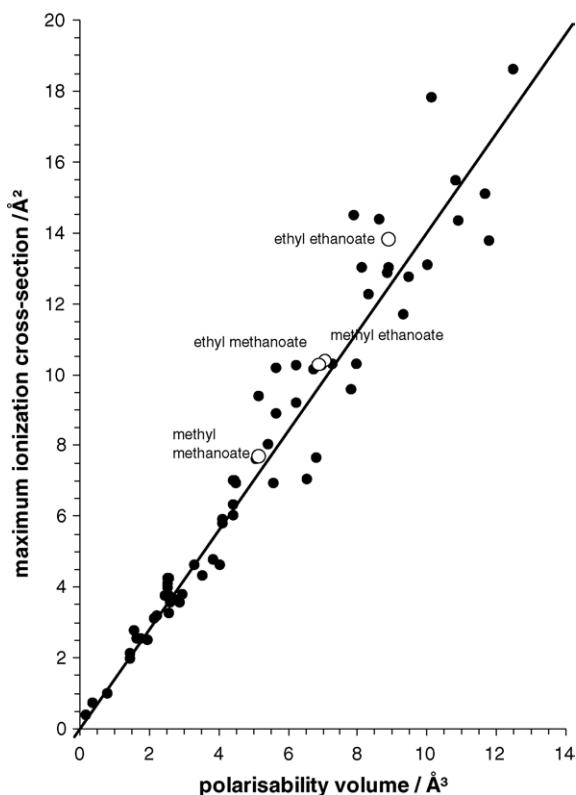


Fig. 4. Plot of the maximum ionization cross-section vs. polarizability volume for a wide range of molecules. Published values for methyl and ethyl methanoate and for methyl and ethyl ethanoate are shown as open circles. The best line fit to the data is given by Eq. (6).

not immediately apparent. In regard to the experiments, measurements of the cross-section for each ester as a function of electron energy was preceded and followed by measurements on  $N_2$  and the deviation from the published “recommended”

Table 1

Experimental and calculated (BEB) maximum total ionization cross-sections for the esters expressed in units of  $\text{\AA}^2$  ( $1 \text{\AA}^2 = 1 \times 10^{-20} \text{ m}^2$ )

Molecule		$\sigma_{\max}$ (experimental)	$\sigma_{\max}$ (BEB)
Methanoates (formates)			
$\text{CH}_3\text{OC(O)H}$	MeM	7.6	6.9
$\text{C}_2\text{H}_5\text{OC(O)H}$	EtM	10.4	9.3
$n\text{-C}_3\text{H}_7\text{OC(O)H}$	$n\text{-PrM}$	13.6	11.7
$i\text{-C}_3\text{H}_7\text{OC(O)H}$	$i\text{-PrM}$	13.0	11.7
$n\text{-C}_4\text{H}_9\text{OC(O)H}$	$n\text{-BuM}$	15.6	14.1
$i\text{-C}_4\text{H}_9\text{OC(O)H}$	$i\text{-BuM}$	15.6	14.1
$n\text{-C}_5\text{H}_{11}\text{OC(O)H}$	$n\text{-AM}$	18.8	16.4
Ethanoates (acetates)			
$\text{CH}_3\text{OC(O)CH}_3$	MeE	10.5	9.2
$\text{C}_2\text{H}_5\text{OC(O)CH}_3$	EtE	13.8	11.7
$n\text{-C}_3\text{H}_7\text{OC(O)CH}_3$	$n\text{-PrE}$	15.7	14.1
$i\text{-C}_3\text{H}_7\text{OC(O)CH}_3$	$i\text{-PrE}$	15.2	14.1
$n\text{-C}_4\text{H}_9\text{OC(O)CH}_3$	$n\text{-BuE}$	18.3	16.6
$i\text{-C}_4\text{H}_9\text{OC(O)CH}_3$	$i\text{-BuE}$	18.3	16.6
$s\text{-C}_4\text{H}_9\text{OC(O)CH}_3$	$s\text{-BuE}$	18.2	16.6
$t\text{-C}_4\text{H}_9\text{OC(O)CH}_3$	$t\text{-BuE}$	18.5	16.6
$n\text{-C}_5\text{H}_{11}\text{OC(O)CH}_3$	$n\text{-AE}$	20.9	19.0

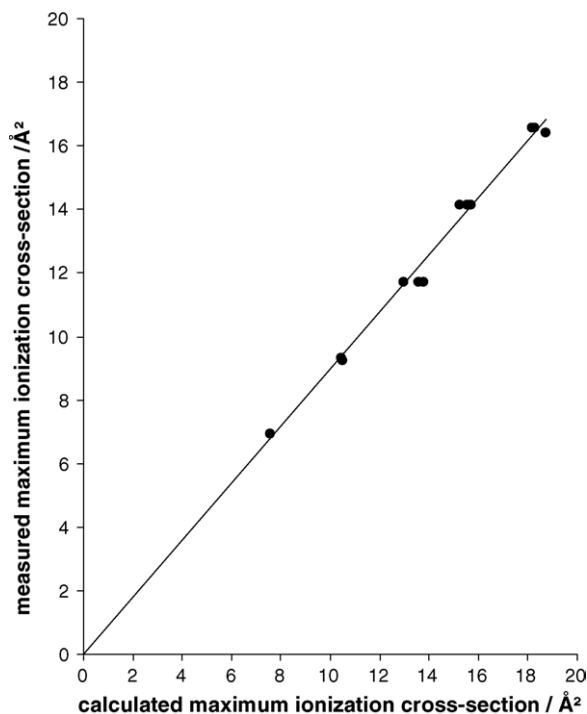


Fig. 5. Plot of the experimental vs. calculated (BEB) maximum ionization cross-sections. The best line fit to the data is given by Eq. (7).

value of  $2.51 \text{\AA}^2$  [9] was never more than a few percent. Measurements for  $\text{SF}_6$  were also made as a cross-check on accuracy with a mean value of  $7.10 \text{\AA}^2$  ( $\pm 4\%$ ) recorded in this work. A review of electron interactions with  $\text{SF}_6$  by Christophorou and Olthoff [29] recommends a  $\sigma_{\max}$  value of  $6.97 \text{\AA}^2$  ( $\pm 7\%$ ) based on the measurements of Rapp and Englander–Golden [30] between threshold and 300 eV, in good accord with the absolute values measured in this instrument.

#### 4. Conclusion

Total absolute ionization cross-sections from 20 to 285 eV have been measured for the  $\text{C}_2$  to  $\text{C}_6$  methanoates and the  $\text{C}_3$  to  $\text{C}_7$  ethanoates, including all isomers. A correlation between the maximum ionization cross-section and the number of skeletal carbons for the esters and the alcohols may be used to predict cross-sections. In addition, a correlation between the maximum ionization cross-section for a wide range of molecules and the polarizability volume can be used to estimate values for polarizability volume when ionization cross-sections are available. Cross-sections measured in this report and those calculated using the BEB theory agree to within better than 10% with the measured values being consistently higher than the calculated values.

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