Eur. Phys. J. D **20**, 441–444 (2002)
DOI: 10.1140/epjd/e2002-00140-1

THE EUROPEAN PHYSICAL JOURNAL D

Low energy electron attachment to formic acid

A. Pelc[1,a], W. Sailer[1], P. Scheier[1], N.J. Mason[1,2], and T.D. Märk[1,3,b]

[1] Institut für Ionenphysik der Leopold Franzens Universität, Technikerstrasse 25, 6020 Innsbruck, Austria
[2] Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK
[3] Department of Plasmaphysics, Comenius University, 84248 Bratislava, Slovak Republic

Received 23 January 2002 and Received in final form 9 February 2002

Abstract. Using a high resolution electron energy monochromator low energy electron attachment to formic acid is studied for the first time by means of mass spectrometric detection of the product anions. The largest dissociative electron attachment (DA) cross-section produces $HCOO^-$+H with weaker channels for OH^- and O^- becoming apparent at higher incident energies.

PACS. 34.80.Ht Dissociation and dissociative attachment by electron impact – 87.50.Gi Ionizing radiations (ultraviolet, X-rays, γ-rays, ions, electrons, positrons, neutrons, and mesons, etc.) – 82.80.Ms Mass spectrometry (including SIMS, multiphoton ionization and resonance ionization mass spectrometry, MALDI)

1 Introduction

Formic acid (H_2CO_2 structured as HCOOH) is the simplest organic acid. It occurs naturally for example in ants and in the fruit of the soaptree and is also formed as a byproduct in the atmospheric oxidation of turpentine. The principal commercial source is sodium formate, which is prepared by the reaction of carbon monoxide and sodium hydroxide under pressure and heat. Formic acid is used in leather manufacture to control pH, as well as in the acid dyeing of some leathers; in the latter case, causing the dye to fix on the leather.

Recently formic acid has been identified as being present in the interstellar medium (ISM) [1,2] and been identified in the coma of Hale-Bopp comet [3,4]. It has therefore been suggested that it may be a key compound in the formation of biomolecules such as acetic acid (CH_3COOH) and glycine (CH_3COONH_2) in the ISM. Glycine is the simplest biologically important amino acid since all that is needed to form glycine is to combine acetic acid and ammonia. Amino acids are the building blocks of proteins and DNA, hence should it be possible to understand the formation mechanisms of amino acids in space, it may be possible to identify those regions in space where more complex, biologically important molecules might be located and thence where the conditions for the development of life exist. Interstellar dust grains – the seeds for the formation of planetary systems – are also thought to play a crucial role in synthesizing complex molecular species like formic acid, acetic acid and glycine on the early Earth to help start prebiotic organic chemistry. However we know remarkably little about the stability of these molecules to either UV radiation or electron bombardment, both prevalent in the interstellar medium and the Earth's atmosphere.

Moreover, it is now generally considered that the types of primary damage induced in DNA by ionising radiation leading to the most significant biological effects are double-strand breaks (DSB) and clustered lesions. Clustering of strand breaks and base damages formed where radiation tracks cross the DNA molecule are believed to have the greatest significance, a view is supported by experimental evidence coupled with information from modelling studies. The genotoxic effects of ionising radiation (α, β, γ, ions) in living cells are produced not only by the direct impact of the primary high energy projectiles but as demonstrated very recently by Sanche and co-workers [5] mutagenic, recombinogenic and other potentially lethal DNA lesions (double strand breaks) are also induced by secondary species generated by the primary ionising radiation, *e.g.*, free electrons with low energies, typically below about 20 eV. Therefore, it is recognised that radiation action in biomolecules cannot be described solely by the interaction of the primary encounter between radiation and the molecule involved, but that the simultaneous and consecutive action of the primary, secondary and tertiary species must be included in any quantitative consideration about radiation damage.

Therefore we have initiated an experimental program that will probe the effects of these (secondary) low energy electrons with molecules under isolated conditions prevalent in the single collisions existing in the crossed

---

[a] *Permanent address:* Institute of Physics, Maria Curie-Sklodowska University, Lublin, 20031 Poland.

[b] e-mail: `tilmann.maerk@uibk.ac.at`

molecular beam geometry adopted in the current experiments. These studies will be performed using several selected prototypical biomolecules as targets including simple organic acids (*e.g.* formic acid and acetic acid), simple nitrogen containing hydrocarbons (*e.g.* nitromethane and nitroethane) and the nucleic acid bases such as uracil, bromouracil and chlorouracil. The very recent development, refinement and application of new experimental techniques in our laboratories (*e.g.*, novel types of molecular beam sources, high resolution electron beam and mass spectrometry techniques [6,7]) makes this the ideal time for carrying out a coordinated series of experiments planned to attack the many open questions in this field. In the present report we will present the first results on low energy electron impact obtained from the simplest of the organic acids formic acid (HCOOH) resulting in the production of three fragment anions $HCOO^-$, OH^- and O^-. It is interesting to note that there exist at least two recent theoretical papers on the formic acid/formate anion problem [8,9] which is fundamental in enzymatic activity.

2 Experimental

The high resolution electron attachment spectrometer consists of a molecular beam system, a high resolution trochoidal electron monochromator (TEM) and a quadrupole mass filter with a pulse counting system for analysing and detecting the ionic products. The modified TEM used here has recently been described in detail [10,11]. In summary we use a hairpin filament to produce a high electron current with an electron distribution of 700 meV. Electrons emitted thermally from the filament tip are extracted by an electric field of several V/mm and guided by an axial magnetic field of up to 50 gauss. The magnetic field is produced by two 100 mm solenoids, which are about 250 mm apart. Typical electron emission currents are in the order of several μA. After passing two electrostatic lenses with orifices of 1 mm diameter the beam enters the dispersive element where a weak electrostatic deflection field of about 100 V/m perpendicular to the magnetic field is applied. According to the trochoidal principle the electrons are deflected depending on their kinetic energy in forward direction. Subsequently, at the exit of the dispersive element part of the electron distribution (<150 meV) is allowed to pass through the orifice in the exit electrode. These electrons are then accelerated to the desired energy and enter the collision chamber, where the monochromatic electron beam is crossed by a molecular beam. The anions produced by the electron attachment processes are weakly extracted into a quadrupole mass filter where they can be analyzed and detected. After crossing the collision region the remaining electrons are collected and the electron current is monitored online during the experiment using a picoammeter.

It has been demonstrated in [11] that the very high energy resolution (<10 meV) obtained at energies close to zero eV in the original instrument [12–14] quickly deteriorates to 100 meV with increasing electron energy. An improved instrument has been designed, on the basis of trajectory calculations, that overcomes these deficiencies, with the new monochromator, an energy resolution of 50 meV or better (independent of the electron energy) can routinely be achieved. For the present experiments, the instrument was operated at an FWHM of about 100 to 150 meV which was a reasonable compromise between product ion intensity and incident electron resolution. The energy scale may be calibrated by recording either SF_6^- from SF_6 or Cl^- from CCl_4 which both show very narrow features close to zero eV energy as revealed from ultrahigh resolution (meV) studies of associative and dissociative attachment by means of the laser photoelectron attachment (LPA) method [15,16].

Samples of 98% pure formic acid were obtained from Sigma Aldrich, Wien, Austria and were used after several freeze thaw cycles. After proper mixing of the equilibrium saturated vapour of the liquid sample of HCOOH with the equilibrium saturated vapour of CCl_4 (used for energy and cross-section calibration) the gas was expanded at a pressure of about 15 mbar (measured with a Pirani pressure gauge) through a 20 μm nozzle into the attachment region (resulting in a stagnant target gas pressure of about 10^{-6} mbar) and the whole apparatus was kept at a constant temperature before and during the measurements of about 55 °C. The equilibrium saturated vapour pressure of formic acid consists of more than 95% of hydrogen bonded dimers at room temperature [17], but fragmentation into the monomer is favoured at higher temperatures and reduced pressures [18] thus leading in the present case to a beam without any traces of dimerised formic acid molecules as confirmed by measuring the positive ion mass spectrum following electron impact ionisation of the neutral target.

Absolute calibration of the presently measured relative attachment cross-sections (anion yields *versus* electron energy) was carried out by measuring several times the ratio of the anion current for the production of $HCOO^-$ from HCOOH at the peak value of the 1.3 eV resonance and the anion current for the production of Cl^- from CCl_4 at the peak value of the 0.8 eV resonance. Using the measured pressure ratios for the gas mixture prior to expansion (and assuming similar ratios in the ion source) and the well known cross-section [13,16] of 5×10^{-20} m^2 at 0.8 eV for the production of Cl^- from CCl_4 yields an estimate for the cross-section for the production of $HCOO^-$ from HCOOH at the peak value of the 1.3 eV resonance of $(1.7 \pm 0.6) \times 10^{-22}$ m^2.

3 Results and discussion

Electron impact with HCOOH in the electron energy range 0–10 eV generates three anionic fragments $HCOO^-$, OH^- and O^- (Figs. 1–3) with intensity ratios (as monitored by the count rate at the highest peak of the respective cross-section curves) of 240:10:1. The present relative cross-section data of $HCOO^-$ have been calibrated (see above) by using the absolute data for the total cross-section for CCl_4 reported in references [13,16], the OH^- and O^- data by using the measured intensity ratios.

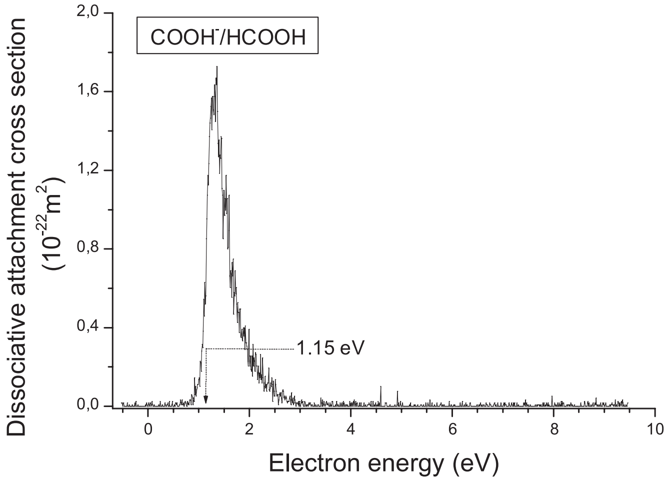

Fig. 1. Formation of negative ions $HCOO^-$ by dissociative electron attachment to formic acid. The pressure in the apparatus was 10^{-6} mbar and electron energy spread was about 140 meV. For absolute calibration with the total cross-section data for CCl_4 of [13,16] see text.

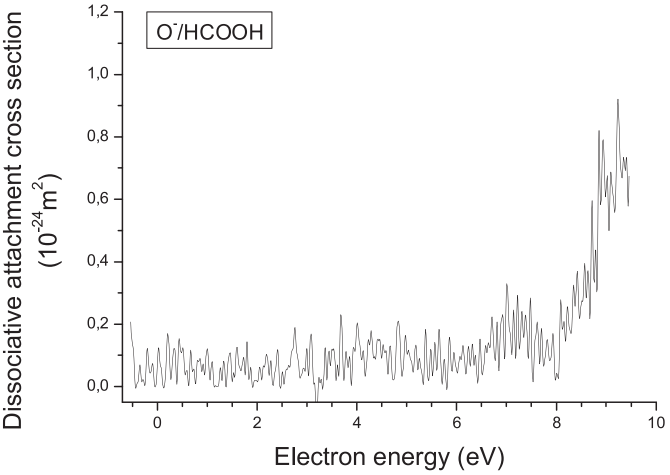

Fig. 3. Formation of negative ions O^- by dissociative electron attachment to formic acid. The pressure in the apparatus was 10^{-6} mbar and electron energy spread was about 140 meV.

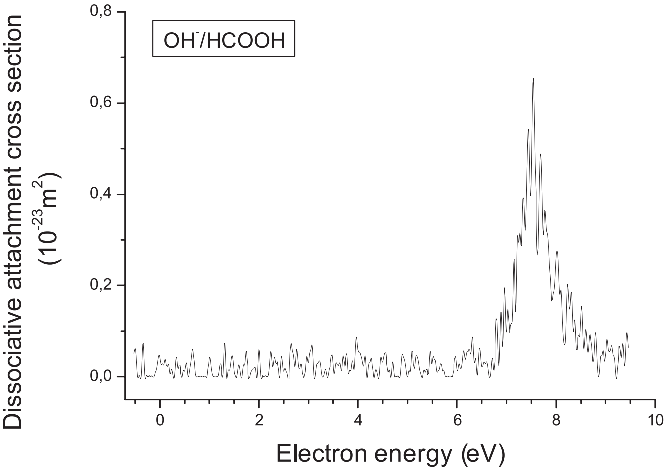

Fig. 2. Formation of negative ions OH^- by dissociative electron attachment to formic acid. The pressure in the apparatus was 10^{-6} mbar and electron energy spread was about 140 meV.

The major channel is $HCOO^-$ with anion production observed over a narrow energy range between 1 and 3 eV peaking at about 1.3 eV. Smaller signals are observed for OH^- around 7.5 eV and for O^- around and above 7.5 eV.

We assign the observed anion signals to the following dissociative electron attachment (DA) reactions

$$e^-(\approx 1.3\ \text{eV}) + \text{HCOOH} \rightarrow \text{HCOO}^- + \text{H}, \quad (1a)$$

$$e^-(\approx 7.5\ \text{eV}) + \text{HCOOH} \rightarrow \text{OH}^- + \text{HCO}, \quad (1b)$$

$$e^-(\approx 7.5\ \text{or}\ 9.2\ \text{eV}) + \text{HCOOH} \rightarrow \text{O}^- + \text{HCOH}. \quad (1c)$$

The yield of $HCOO^-$ is characteristic of resonance formation in the parent molecule HCOOH, forming a temporary anion $HCOOH^-$ which may subsequently decay by either dissociation to $HCOO^-$ or auto-detachment leaving the parent molecule vibrationally excited. However to date there have been no experiments to probe the vibrational excitation of formic acid except for preliminary results of an earlier electron transmission experiment (reported at a conference) [18] where a fine structure was observed for a resonance state excited at around 1.3 eV. This structure has been attributed to OCO vibrational bending in the $HCOOH^-$ temporary parent anion. According to [18] the electronegativity of the OH substituent influences the energy, lifetime and excited levels of the π^* C=O resonance with the presence of the two lone pairs making the π^* CO double bond not completely localised but rather involving a charge transfer from the carboxyl and hydroxyl oxygen to the carbon atom. The observed cross-section for production of $HCOO^-$ is characterised by a very sharp onset at around 1.15 ± 0.1 eV, similar to that observed in H^- from H_2 [19]. This onset is consistent with the thermodynamic threshold for formation of $HCOO^-$ from the parent HCOOH of 1.30 ± 0.13 eV derived from the difference between the bond dissociation energy $D(\text{HCOO–H}) = 4.47$ eV (calculated from enthalpy of formation [20]) and the electron affinity $EA(\text{HCOO}) = 3.17 \pm 0.13$ eV [20].

The formation cross-sections for both OH^- and O^- are at least an order of magnitude weaker than that for $HCOO^-$ and these ions are only formed at higher incident electron energies. Both cross-sections suggest resonance-like features which may be coupled to excited valence states of the parent molecule. Unfortunately at present there is little experimental information on the excitation energies of either the valence states or Rydberg states of formic acid [21,22] and no electron scattering experiment has been performed at these energies to locate resonances of the parent $HCOOH^-$ anion. Such experiments should be performed if we are to understand the dissociation dynamics of formic acid by electron impact.

4 Conclusions

Dissociative electron attachment to formic acid has been studied for the first time. The largest dissociative electron attachment (DA) cross-section produces $HCOO^-$+H with weaker channels for OH^- and O^- becoming apparent at higher incident energies. These experiments reveal the need for a more comprehensive investigation of electron scattering from formic acid including total scattering cross-sections; vibrational excitation (to reveal resonance formation) and a study of the electronic states of the molecule. It would then be useful to study the larger acids (*e.g.*, acetic acid) to investigate trends. Such experiments may provide important information on the mechanisms of selective bond breaking by electron impact that may be of relevance to (i) understanding the formation of such molecules on grains in the interstellar medium and hence being of direct interest for radioastronomy and for exobiology studies and may also (ii) elucidate biological effects of ionising radiation in living cells if carried out under corresponding conditions (*e.g.*, using aggregates of these acids as targets for such investigations).

This work has been supported in part by the FWF, ÖAW, and ÖNB, Wien, Austria and the EU Commission, Brussels. One of us (NJM) thanks the UK EPSRC for financial support.

References

1. J. Ellder, P. Friberg, A. Hjalmarson, B. Hoeglund, W.M. Irvine, L.E.B. Johansson, H. Olofsson, G. Rydbeck, O.E.H. Rydbeck, Astrophys. J. Lett. **242**, L93 (1980)
2. W.M. Irvine, P. Friberg, N. Kaifu, Y. Kitamura, K. Kawaguchi, Astrophys. J. **342**, 871 (1989)
3. S.D. Rodgers, S. Charnley, Month. Not. Roy. Astron. Soc. **320**, L61 (2001)
4. D. Bockelee-Morvan, D.C. Lis, J.E. Wink, D. Despois, J. Crovisier, R. Bachiller, D.J. Benford, N. Biver, P. Colom, J.K. Davies, E. Gerard, B. Germain, M. Houde, D. Mehringer, R. Moreno, G. Paubert, T.G. Phillips, H. Rauer, Astron. Astrophys. **353**, 1101 (2000)
5. B. Boudaiffa, P. Cloutier, D. Hunting, M.A. Huels, L. Sanche, Science **287**, 1658 (2000)
6. G. Senn, J.D. Skalny, A. Stamatovic, N.J. Mason, P. Scheier, T.D. Märk, Phys. Rev. Lett. **82**, 5028 (1999)
7. T. Fiegele, G. Hanel, I. Torres, M. Lezius, T.D. Märk, J. Phys. B **33**, 4263 (2000)
8. A.J. Beveridge, J. Mol. Struct. **453**, 275 (1998)
9. G.A. Kumar, Y. Pan, C.J. Smallwood, M.A. McAllister, J. Comp. Chem. **19**, 1345 (1998)
10. V. Grill, H. Drexel, W. Sailer, M. Lezius, T.D. Märk, J. Mass Spectrom. **36**, 151 (2001)
11. V. Grill, H. Drexel, W. Sailer, M. Lezius, T.D. Märk, Int. J. Mass Spectrom. **205**, 209 (2001)
12. S. Matejcik, A. Kiendler, P. Stampfli, A. Stamatovic, T.D. Märk, Phys. Rev. Lett. **77**, 3771 (1996)
13. S. Matejcik, G. Senn, P. Scheier, A. Kiendler, A. Stamatovic, T.D. Märk, J. Chem. Phys. **107**, 8955 (1997)
14. S. Matejcik, A. Kiendler, P. Stampfli, A. Stamatovic, T.D. Märk, J. Chem. Phys. **111**, 3548 (1999)
15. D. Klar, M.-W. Ruf, H. Hotop, Chem. Phys. Lett. **189**, 448 (1992)
16. D. Klar, M.-W. Ruf, H. Hotop, Int. J. Mass Spectrom. **205**, 93 (2001)
17. W. Waring, Chem. Rev. **52**, 171 (1952)
18. M. Tronc, M. Allan, F. Edard, Abstract of contributed papers, *XVth XV ICPEAC*, Brighton, 1987, p. 335
19. H. Drexel, G. Senn, T. Fiegele, P. Scheier, A. Stamatovic, N.J. Mason, T.D. Märk, J. Phys. B **34**, 1415 (2001)
20. NIST Chemistry Webbook, NIST Standard Reference Database Number 69, February 2000, edited by W.G. Mallard, P.J. Linstrom, National Institute of Standards and Technology, Gaithersburg MD 20899 (`http://webbook.nist.gov/`)
21. D. Demoulin, Chem. Phys. **17**, 471 (1976)
22. S.D. Peyerimhoff, P.S. Skell, D.D. May, R.J. Buenker, J. Am. Chem. Soc. **104**, 4515 (1982)