Complex internal rearrangement processes triggered by electron transfer to acetic acid

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Abstract. We present negative ion formation from collisions of 100 eV neutral potassium atoms with acetic acid (CH_3COOH) and its deuterated analogue molecules (CH_3COOD, CD_3COOH). From the negative ion time-of-flight (TOF) mass spectra, OH^- is the main fragment detected accounting on average for more than 25% of the total anion yield. The complex internal rearrangement processes triggered by electron transfer to acetic acid have been evaluated with the help of theoretical calculations at the DFT levels explaining the fragmentation channel yielding OH^-.

1. Introduction

The biological effects of radiation induced reactions are known to be essentially produced by the secondary species generated along the radiation track. The vast majority of these species are secondary electrons (< 20 eV) [1, 2], which are found to be more efficient producing degradation than the primary radiation. These landmark studies [2] have shown the effectiveness of low-energy electrons (LEE) to produce single and double strand breaks in DNA, which were rationalised on the basis of single electron interactions with DNA subunits through formation of transient negative ions. Even at sub-excitation energies, LEEs are extremely efficient in damaging DNA owing to their ability to promote fragmentation through the decomposition of its building blocks [2]. It is now well-established that the degradation mechanism is described at the molecular level. As such, the relevance of negative ion chemistry of isolated biological molecules can provide valuable insights on the underlying molecular mechanisms, with the uttermost need to evaluate such processes within the physiological environment.

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Negative ion chemistry can be explored not only in the context of free electron interactions, but from the point of view of atomic collisions, where in the latter, an electron is transferred from a donor projectile to the target molecule inducing different fragmentation pathways than those attained in free electron attachment experiments (e.g. ref. [3]). The presence of free electrons in the physiological environment is somewhat of an insufficient model on how electron-induced reactions may occur. As such, studies on electron transfer seem to be more attuned and can provide valuable insight of the underlying mechanisms that lead to molecular decomposition. Here we focus our interest in atom-molecule collisions, where a weakly bound valence electron is transferred from the projectile (neutral potassium atom) to the bio target molecule.

The electron transfer process happens when electrons follow adiabatically the nuclear motion in the vicinity of the crossing of the stationary non-perturbed states [4], i.e. the covalent and the ionic diabatic states (from the crossing of the covalent and the ionic diabatic potential surfaces, see Figure 1). For simplicity, let us consider a diatomic molecule, although for polyatomics hyperdimensional surfaces must be similarly considered. The ionic surface lies above the covalent surface, the endoergicity (ΔE in units of eV) at large atom-molecule distances being:

$$\Delta \mathrm{E} = IE(\mathrm{K}) - EA(ABC) \qquad (1)$$

where K stands for the potassium atom and *ABC* a molecule. However, due to the Coulombic interaction there is a crossing point, R_c, for which both stationary non-adiabatic potential energy surfaces have the same value [4]. R_c, is given by [5]:

$$R_c = 14.41 / \Delta \mathrm{E}\ [\text{Å}] \qquad (2)$$

During the collision process and near that crossing (R_c), there can be a perturbation of the stationary states induced by the projectile or target nuclear motion leading to an adiabatic coupling. This leads, after the collision path, to the formation of a positive ion K^+ and a molecular temporary negative ion (TNI) allowing access to parent molecular states which are not accessible in free electron attachment experiments [3, 5, 6–8].

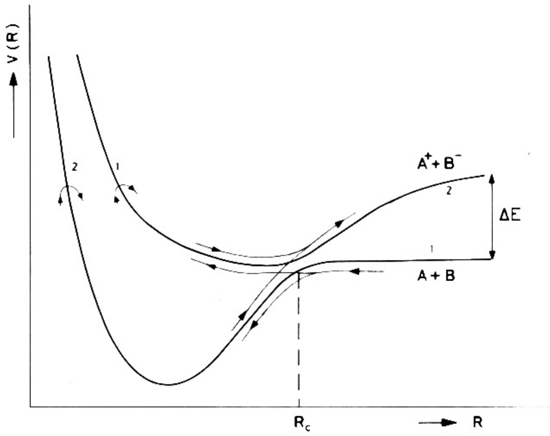

Figure 1. Schematic potential energy curves of two adiabatic states $V_{1\text{-}2}(R)$ and $V_{2\text{-}1}(R)$ as a function of the internuclear distance *R*(A-B), and trajectories with adiabatic and non-adiabatic transitions (diabatic states 1-1 (covalent) and 2-2 (ionic)); R_c stems for crossing radius and ΔE for the endoergicity. Adapted from [9].

In effect, even if the free negative molecular ion is unstable towards autodetachment, in the collision complex it can be stabilized at distances shorter than the crossing between the two potential energy surfaces. This is due to the attractive interaction with the positive ion (K^+) [8]. The negative molecular ion lifetime will depend on the collision time and not only on the natural lifetime of the resonant anionic state. Indeed, when the parent negative ion has a lifetime longer than the fragmentation times, the excess energy may be distributed over the available internal degrees of freedom and so influence the type of fragmentation ions formed in the collision.

We note an extensive work on dissociative electron attachment studies [10] (and references therein), whereas those pertaining to electron transfer from atom-molecule collision experiments are somewhat scarce, with literature only available for pyrimidine-like bases [3, 11–15], their halogenated derivatives [7], sugar unit surrogates [16–18] and pyrimidine-sugar uridine molecules [19]. Relevant electron transfer studies have been also reported for short chain amino acids [20, 21].

The present work is part of a wider research programme on electron transfer in atomic collisions aimed at understanding low-energy electron damage to DNA/RNA-constituent molecules. Some previous studies on pyrimidine bases and their derivatives have shown significant differences in the fragmentation patterns against dissociative electron attachment (DEA) and electron transfer experiments [3, 8], which for the latter have been attributed to the role of the potassium cation (K^+) post-collision delaying autodetachment.

Here we present a set of data on negative ion time-of-flight (TOF) mass spectra on our recent investigations regarding OH^- formation from collisions of neutral potassium atoms with acetic acid molecules and its deuterated analogues. The dissociation mechanisms have been thoroughly investigated by performing comprehensive experiments on its deuterated analogues, CH_3COOD and CD_3COOH together with quantum chemical calculations.

2. Experimental setup

The experimental setup used to obtain the negative ion time-of-flight (TOF) mass spectra has been described elsewhere [3, 8]. Briefly, an effusive molecular beam crosses a primary beam of fast neutral potassium (K) atoms. K^+ ions produced in a potassium ion source were accelerated to 100 eV, before passing through an oven where they resonantly charge exchange with neutral potassium to produce a beam of fast (hyperthermal) atoms. Residual ions from the primary beam are removed by electrostatic deflecting plates outside the oven. The intensity of the neutral potassium beam was monitored using a Langmuir-Taylor ionisation detector, before and after the TOF mass spectra collection. Ionic currents of the order of a few hundreds of pA were detected at 100 eV lab frame collision energy. The effusive beam of acetic acid molecules was then introduced into a 1 mm diameter source where it was crossed with the neutral hyperthermal potassium beam between two parallel plates at 1.2 cm mutual separation. The anions produced were extracted by a 220 Vcm^{-1} pulsed electrostatic field. The typical base pressure in the collision chamber was 1×10^{-5} Pa and the working pressure upon sample admission was 1×10^{-3} Pa. Mass spectra were obtained by subtracting the background signal from the sample measurements. TOF mass spectra calibration was carried out on the basis of the well-known anionic species formed after potassium collisions with the nitromethane molecule [8]. This allows for safe mass assignment, even when the width of the peaks is larger than 1 m/z.

The samples were purchased from Sigma-Aldrich with a minimum purity of ≥ 99%. They were used as delivered and degassed by a repeated freeze-pump-thaw cycles.

3. Results and discussion

Acetic acid and formic acid have been studied by DEA experiments [22–24] where the main focus was given on the dehydrogenated parent anion formation. Meanwhile, DEA theoretical calculations of Rescigno *et al.* [25] have shown that upon electron capture, formic acid proceeds through a $\pi^*_{C=O}$ resonance leading to OH excision. Such mechanism is only possible if the nuclear wave packet survives long enough to diabatically couple with σ^*_{OH} leading therefore to dissociation. Notwithstanding, the calculations of Gallup *et al.* [26] on the DEA cross sections for formic acid, suggest that the mechanism of H loss involves electron capture into a σ^*_{OH} orbital only, where the prevalent π^*/σ^* coupling of Rescigno *et al.* [25] is not the main dissociation mechanism. The recent experimental data of Allan *et al.* [24] on formic acid, lends support to Gallup *et al.*'s [26] mechanism. We note experimental evidence for the role of the π^*_{CO} orbital in electron transfer to gas phase oriented acetic acid molecules, where intramolecular electron transfer allows accessing σ^*_{OH} orbital leading to O–H bond cleavage [27]. The acetic acid and its deuterated analogues negative ion TOF mass spectra obtained for 100 eV potassium collision energies in the lab frame are presented in Figure 2(a)–2(c), with peak assignments in Table 1. A brief analysis of these data shows that the most abundant fragments are assigned to OH^- (17 m/z), followed by CH_3COO^- (59 m/z) / CD_3COO^- (62 m/z) and O^- (16 m/z). Other less intense fragment anions have been detected, where we also note that there is no evidence of parent anion formation. It is relevant that such anion formation was not reported in DEA experiments [22, 23].

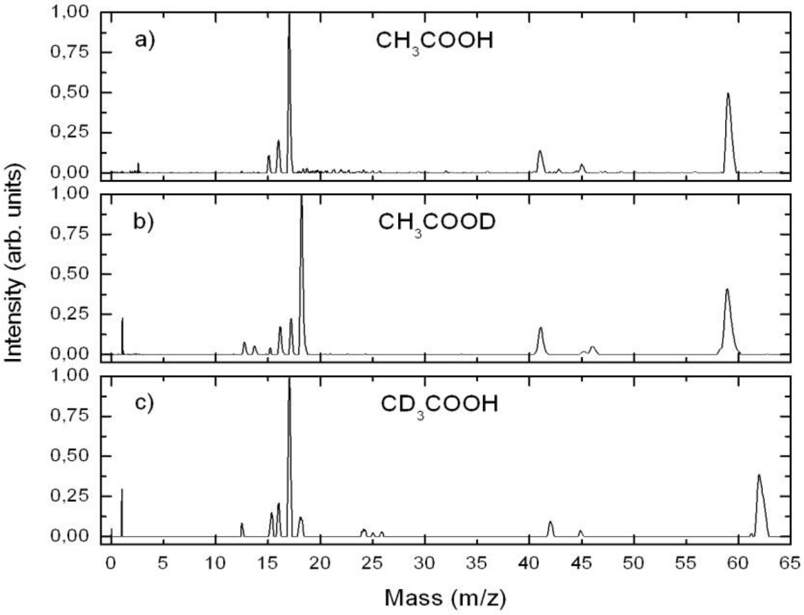

Figure 2. Negative ions time-of-flight mass spectra in collisions of potassium atoms with acetic acid and its deuterated analogues at 100 eV.

(m/z)	CH_3COOH	CH_3COOD	CD_3COOH
	Proposed anionic assignment		
62	–	–	CD_3COO^-
59	CH_3COO^-	CH_3COO^-	–
45	$HCOO^-$	$HCOO^-$	$HCOO^-$
42	–	–	$CDCO^-$
41	$CHCO^-$	$CHCO^-$	–
18	–	OD^-	OD^- / CD_3^-
17	OH^-	OH^-	OH^-
16	O^-	O^-	O^-
15	CH_3^-	CH_3^-	CDH^-
1	H^-	H^-	H^-

Table 1. Assignment of TOF mass spectra anionic species formed in collisions of potassium atoms with acetic acid and its deuterated analogues at 100 eV.

The dissociation mechanism in potassium collisions yielding a neutral H atom and CH_3COO^- / CD_3COO^- anions can be regarded as a pseudodiatomic behaviour. In this context, we recall Equation (1) and for large potassium-molecule values, the van der Waals and induction forces can be neglected and consequently the covalent potential is zero and the ionic potential is purely Coulombic. If this approximation holds, R_c is given by Equation (2), where ΔE is expressed in eV. Taking CH_3COOH calculated adiabatic electron affinity as -1.302 eV [28], the value for R_c is found at ~ 2.6 Å. The corresponding total cross sections for ion-pair formation will be of the order of $\pi R_c{}^2$, which is much larger than the corresponding gas kinetic cross sections. Here we are particular interested to explore the complex internal rearrangement process yielding OH^- formation and so we restrict ourselves to the discussion on this fragment only. However, a thoroughly discussion on the other fragment anions formation as a function of the collision energy, which is far beyond the scope of this contribution, is due to appear soon [29].

OH^- is the prevalent fragment anion in collisions of potassium atoms with acetic acid and its deuterated analogues molecules (Figure 2). A close inspection of Table 1 reveals that such anion formation in K – CH_3COOD collisions does not result from a direct dissociation process but rather through a complex mechanism, which may certainly involve internal rearrangement in the precursor TNI yielding OH^- formation. In order to infer the underlying molecular mechanism yielding the hydroxyl anion formation, we have performed comprehensive DFT calculations. For further details on the theoretical methods and thoroughly discussion, see reference [30].

Neutral acetic acid shows two limiting conformations of the COOH terminal group (see **a** and **b** in Figure 3), where **a** is 0.2 eV more stable than **b**. However, upon electron capture, this order is reversed and an energy difference of 0.1 eV is found between the two anionic conformers, schematically shown in Figure 3.

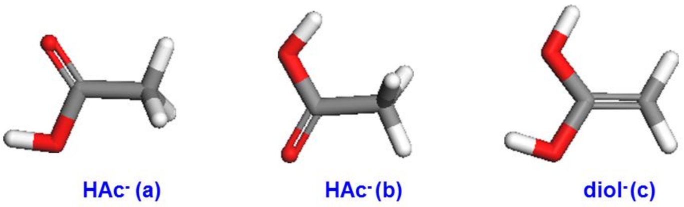

Figure 3. Geometries of the two lowest energy conformers of acetic acid radical anion and the diol ($CH_2COHOH^{\bullet-}$) structure. For further details see ref. [30]

In the electron transfer process from the neutral K atom to the acetic acid molecules, the single occupied molecular orbital (SOMO) is mainly localized on the OH and the CH_3 groups. Direct cleavage of the C-OH bond leads to $OH^\bullet$ (radical) formation. This mechanism was discarded since no OH radical experimental observed. Two different pathways might result in the hydroxyl anion formation, but calculations have shown that the lowest energy pathway involves H atom release from the COOH group, prior to subsequent intramolecular rearrangement to eliminate OH^- (Figure 4). The production of a reactive H atom and the negative carboxylate anion in the first step occurs with an energy barrier of 0.5 eV. This is followed by an intramolecular H transfer from the CH_3 group to CO, resulting in an intermediate transition state ($TS_{I1/I2}$) at 2.7 eV. Next, the diol structure is formed by addition of the free hydrogen atom to the CO group (barrierless process, 0.1 eV) and finally OH^- and $CH_2COH^\bullet$ are formed through fragmentation of a C-OH bond (1.36 Å). This result lends support to the TOF mass spectra obtained in collisions of potassium atoms with acetic acid and its deuterated analogue molecules. The alternative mechanism proceeds by H transfer from CH_3 to form a diol structure followed by OH bond rupture, with a highest barrier of 2.9 eV [30]. A close comparison between the two pathways reveals that the global barriers differ by a small amount (0.2 eV), meaning that there is a kinetically favoured route. In both cases, the energy barrier corresponds to an intramolecular rearrangement where H is transferred from the CH_3 group to the CO group.

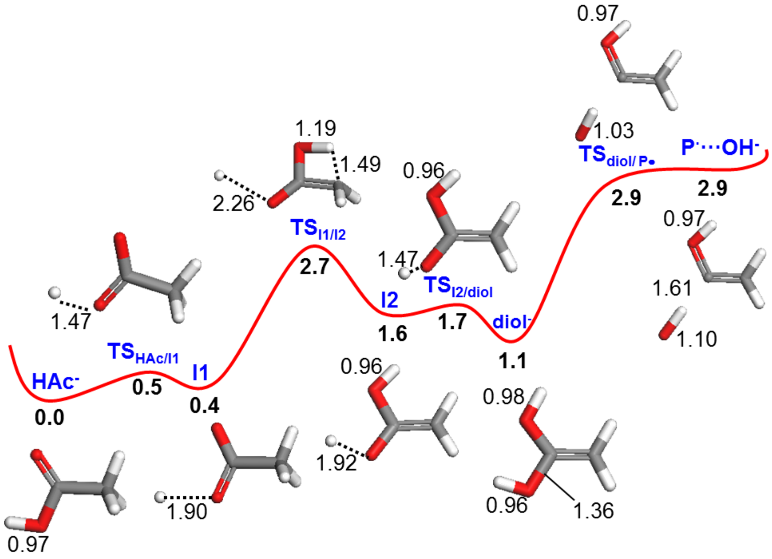

Figure 4. Lowest energy profile (eV) for OH^- formation from CH_3COOH^- (distances in Å). Adapted from ref. [30]

Although calculations support the pathway in Figure 4 as the most favourable mechanism yielding OH^- formation, experimental results (Figure 2) suggest a competition with the alternative one, in agreement with the small difference in the calculated barriers. OH^- formation from CD_3COOH seems to be mostly supported by the pathway in Figure 4, with H atom abstraction from COOH and subsequent intramolecular rearrangement to eliminate the hydroxyl anion. However, OH^- formation from CH_3COOD is mostly described through the other pathway. In both cases, we note that the diol structure is a transient species formed in these complex intramolecular rearrangement processes leading to fragmentation.

4. Conclusions

The present work provides a combined experimental and theoretical study on negative ion formation in collisions of potassium atoms with acetic acid and its deuterated analogue molecules. We note that, in the temporary negative ion (TNI), a diol transient structure is formed through a combined complex internal rearrangement mechanism, with an H atom being transferred either from the CH_3 or from the COOH groups. These will lead to a considerable internal energy conversion through the transition states, ending in OH^- elimination.

5. Acknowledgments

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