PHOTOFRAGMENTATION OF GASEOUS HCOOH AT THE O 1s EDGE

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ABSTRACT

Time of flight mass spectrometry with multi-ion coincidence detection has been used to investigate ionic photofragmentation of formic acid following O 1s excitation and ionization. Multi-ion coincidence spectra (PEPICO and PEPIPICO), branching ratios (BR) and partial ion yields (PIY) are reported. The multi-ion coincidence detection is used to identify the dissociation channels following O 1s excitation and to explore the dynamics of fragmentation. The fragmentation mechanisms are suggested using two- and three-body decay approximation.

1. INTRODUÇÃO

Inner-shell excitation and associated spectroscopies of ionic fragmentation of inner-shell states are site specific probes of electronic and geometrical structure and photoionization dynamics [1,2]. The combination of tunable synchrotron radiation and multi-ion coincidence time-of-flight mass spectrometry enables studies of the excitation and ionic fragmentation of inner-shell excited and ionized molecules. Auger decay of these states is an efficient source of multiply charged ions. The charge separation and fragmentation of those species can be studied by photoelectron-photoion coincidence (PEPICO), photoion-photoion coincidence (PIPICO), and photoelectron-photoion-photoion coincidence (PEPIPICO) techniques. Related to individual timeof-flight mass spectra, partial ion yield (PIY) can provide additional insights into ionic fragmentation through increased spectroscopic selectivity [3]. PIY spectra, typically derived from branching ratios, extracted from the TOF mass spectra recorded at a sequence of photon energies, give us a broad overview of the fragmentation of each state while multi-ion coincidence techniques are important tools to identify the fragmentation mechanisms involved.

The branching ratio (BR) is defined as the ratio of the yield of a specific ion to the total ion yield. The branching ratio spectra for each ion were derived from the peak areas of the PEPICO spectra measured at a defined range of energies. The PIY spectra were derived by taking the product of the branching ratio and the absolute total ion yield (TIY) signal. Formic acid is the simplest carboxylic acid and is used as a model for other organic acids with more complicated chem-

ical structures [4]. The photofragmentation of the formic acid has been extensively studied following C 1s excitation by photon-stimulated ion-desorption (PSID) [5,6] and in gas phase [7]. Deuterated formic acid has also been used to investigate the core-excited fragmentation mechanisms in both surface [8-10] and gas phase [11] conditions. However, in our knowledge, only one photofragmentation study of formic acid at the O 1s edge [12] has been conducted so far. In this study the ionic fragmentation of gaseous formic acid at O 1s region has been investigated and compared with the literature [12]. The photofragments of this carboxylic acid have been acquired by using tuned synchrotron light and a time-of-flight mass spectroscopy (TOF-MS). PEPICO spectra at K-edge (C 1s and O 1s), partial ion yield (PIY) and branching ratios (BR) spectra of formic acid for all channels are presented.

2. EXPERIMENTAL

The experiments have been performed using the Spherical Grating Monochromator (SGM) beamline at the National Laboratory of Synchrotron Light (LNLS), in Campinas -Brazil. The SGM monochromator works in a 250-1000 eV spectral range, providing maximum photon flux (4.0×10^7) mA) about 800 eV with 100 µm exit slit. The resolving power $(E/\Delta E)$ is about 3000 in a 0.5x0.5 mm spot [13]. High purity sample was obtained commercially from Sigma-Aldrich (99.5% minimum) and purified by removing the air and volatile impurities by a series of freeze-pump-thaw cycles. The vapour above the liquid at room temperature was introduced into the ionization region of the time-offlight apparatus through a leak valve. A stainless steel needle was used to orient the effusive sample jet perpendicular to both TOF entrance and the monochromatized photon beam. The work pressure was maintained at 1.0×10^{-6} mbar during data acquisition. A low sample pressure was used in order to optimize the signal rate while keeping false coincidences to a minimum. The base pressure of apparatus was 2.0x10⁻⁸ mbar.

The time-of-flight apparatus has been described in detail elsewhere [14,15]. Briefly, it consists of a McLaren type space charge focusing instrument [16] in which an electric field of 708 V/cm was applied to extract the photoelectrons and the parent and fragment ions into opposing electron and

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ion detection channels. An additional lens installed after ion extraction grid (-2050 V) was used to focus the positive fragment ions produced at the fragmentation region onto a microchannel plate (MCP) detector in order to achieve 100% efficiency for ions with kinetic energies up to 30 eV.

3. RESULTS AND DISCUSSION

3.1 PEPICO SIGNALS

Figure 1 shows the comparison of the photoelectronphotoion coincidence spectra (PEPICO) in different excitation energies, from pre-edge (280 eV) through *K*-edge region of gaseous formic acid. The assignments of each ion group are indicated at the spectra. Likely, the H⁺ ion is the strongest signal in these spectra at any energy, while the parent ion (HCOOH⁺) is more intense at the pre-edge region than in the *K*-edge region. It is possible to distinguish some groups of ions as a fragmentation dynamics partner. H_XC⁺, OH_X⁺, H_XC₂⁺, COH_X⁺ and COOH_X⁺ (X= 0, 1, 2, 3) ion groups are present in the formic acid fragmentation along pre-edge through *K*-edge region. Table 1 lists the assignments for the PEPICO signals of formic acid along with their mass-to-charge (m/e) ratios.



Figure 1 – Comparison of the PEPICO spectra of formic acid in different excitation energies from pre-edge (280 eV) through *K*-edge region.

Studies about the competition between both H-C and O-H dissociation bonds have been shown that the first breaking bond is at the oxygen atom, even following C1s excitation [17]. In the deuterated DCOOH molecule, the breaking of D-C bond is more energetic than the O-H [18]. In the reaction of fluorine and deuterated DCOOH and HCOOD molecules the HF + DCOO⁻ production is twice than the DF + COOH⁻ at the first reaction and HF + COOD⁻ is the principal product in the second one [19]. These experimental observations suggest that the dissociation of the atom bonded to the oxygen is following by a molecular rearrangement with the migration of the atom bonded to the carbon to the oxygen [20]. Calculations have been shown that the HCOO⁺ ion is more stable than the COOH⁺ [21,22]. The resonance

effect of the carboxylic group and the molecular geometry corroborate to the dissociation at the oxygen atom [23].

Table 1 – Assignments for PEP	ICO signals of formic acid with
mass-to-ch	arge ratios.

8		
m/e	Fragment	
1	H^{+}	
12	C^+	
13	HC^+	
14	CO^{++}	
16	O^+	
17	OH^+	
18	$\mathrm{OH_2}^+$	
28	CO^+	
29 ^a	HCO^+	
30	HCOH^+	
44	COO^+	
45 ^a	HCOO^+	
46	HCOOH^+	

3.2 PARTIAL ION YIELD AND BRANCHING RATIO SPECTRA

Figures 2 and 3 show, respectively, the partial ion yield spectra (PIY) and their associated branching ratios (BR) between 525 and 560 eV for all ions produced after excitation of gaseous formic acid. The total ion yield (TIY) spectrum is also plotted at the top panel to facilitate the identification of possible states for specific fragmentation. The assignments are described in the figure captions [24]. Our photofragmentation results are in good agreement with the literature [12]. Relative to the TIY spectrum of the formic acid, the single yield of the HCO⁺ ion is dramatically enhanced at 532.2 eV (O1s_{C=0} $\rightarrow \pi^*_{C=0}$) and suppressed at 535.4 eV $(O1s_{C-OH} \rightarrow \pi^*_{C=O})$. As discussed elsewhere [12], the bound nature of C=O remains after $O1s_{C=O} \rightarrow \pi^*_{C=O}$ excitation, contributing to the stability of HCO⁺ ion in molecular formic acid. HCOH⁺ and HCOOH⁺ ions are completely suppressed after $O1s_{CO} \rightarrow \pi^*_{CO}$ transition. HCOO⁺ ion is suppressed at 535.4 eV (O1s_{C-OH} $\rightarrow \pi^*_{C=O}$) and enhanced in the O1s continuum. C⁺ and CO⁺ ions are suppressed in the O1s continuum. $\mathrm{COO}^{\scriptscriptstyle +}$ ion shows an inversion in the intensity signal between $O1s_{C=O} \rightarrow \pi^*_{C=O}$ (suppressed) and $O1s_{C-OH}$ $\rightarrow \pi^*_{C=O}$ (enhanced) transitions.

Table 2 presents the branching ratios of single ions for corresponding ionic decay channels at selected energies at the *k*-edge (C1s [11] and O1s). The most intense ion produced at the *k*-edge is H⁺ (50.0% at C1s $\rightarrow \pi^*_{C=0}$ and 28.5% at O1s_{C=0} $\rightarrow \pi^*_{C=0}$). The C⁺, O⁺ and CO⁺ channels show almost the same yield in both C1s and O1s regions. The remarkable change appears to the HCO⁺ channel, that is three times greater at O1s_{C=0} $\rightarrow \pi^*_{C=0}$ excitation than at the C1s $\rightarrow \pi^*_{C=0}$ one. Comparing to the C1s excitation, the number of channels in which hydrogen atom is present after the O1s excitation (HC⁺, OH⁺, HCO⁺, HCOO⁺ and HCOOH⁺) cor-

 $^{^{\}rm a}$ We are not distinguishing between HCO+/COH+ or HCOO+/COOH+. See discussion along the text.

roborates to the bond breaking priority in the H bonded to oxygen, suggesting the site-specific behavior in the dissociation of formic acid in the *k*-edge.



Energy (eV)

Figure 2 – Partial Ion Yield spectra of formic acid at O 1s region. The assignments [24] are: 1- $O1s_{C=0} \rightarrow \pi^*_{C=0}$; 2- $O1s_{C-OH} \rightarrow \pi^*_{C=0}$; 3- $O1s_{C-OH} \rightarrow 3p$; 4- $O1s_{C-OH} \rightarrow \sigma^*_{C-OH}$; 5- $O1s_{C=0} \rightarrow \sigma^*_{C-OH}$.

3.4 PEPIPICO SIGNALS

Figure 4 shows the photoelectron-photoion-photoion coincidence (PEPIPICO) spectra of gaseous formic acid measured at 532 eV (near the $Ols_{C=O} \rightarrow \pi^*_{C=O}$ resonance maximum). Relatively to the photoion-photoion coincidence (PIPICO) signal (not shown), the PEPIPICO spectrum presents a clearly advantage in the assignment of the ion pairs yielded. It means that each ion of the pair is explicitly defined by its flight time.



Figure 3 – Branching Ratios spectra of formic acid at O 1s region. The assignments [24] are: 1- $O1s_{C=O} \rightarrow \pi^*_{C=O}$; 2- $O1s_{C-OH} \rightarrow \pi^*_{C=O}$; 3- $O1s_{C-OH} \rightarrow 3p$; 4- $O1s_{C-OH} \rightarrow \sigma^*_{C-OH}$; 5- $O1s_{C=O} \rightarrow \sigma^*_{C-OH}$.

Table 2 – Branching ratios of single ions for corresponding ionic decay channels comparing C1s and O1s.

	C 1s [Ref. 11]		O 1s [T	O 1s [This work]	
Ion	288.2	320	532.2	550	
	eV^a	eV^b	eV^{c}	eV^b	
H^+	50.0	55.5	25.8	31.1	
C^+	7.6	8.2	8.5	8.6	
HC^{+}	-	-	4.7	3.6	
O^+	15.2	17.8	15.3	18.1	
OH^+	-	-	5.2	8.4	
CO^+	10.1	7.7	13.5	11.3	
HCO^+	6.5	3.6	20.5	10.3	
COO^+	-	-	1.6	2.1	
HCOO^{+}	-	-	1.5	2.8	
Others	10.6	7.2	3.3	3.6	

 ${}^{a}C1s \rightarrow \pi^{*}{}_{C=0}.$

^bContinuum.

 $^{\circ}\text{Ols}_{C=O} \rightarrow \pi^{*}{}_{C=O}$



Figure 4 – Photoelectron-photoion-photoion coincidence (PEPIPICO) spectra of gaseous formic acid measured at 532 eV.

Figure 5 shows the 2D ion pair projections of PEPIPICO signals acquired at 532 eV (near the $O1s_{C=O} \rightarrow \pi^*_{C=O}$ resonance maximum). It is well known that the shape and the slope of the 2D ion pair projection of PEPIPICO suggest the fragmentation dynamics, each one as a two-body dissociation (*Charge Separation* – CS), three-body dissociation (*De*ferred Charge Separation – DCS; Secondary Decay – SD; Concerted Dissociation - CD) and four-body dissociation (DCS; SD; Secondary Decay after a Deferred Charge Separation – SDDCS; Secondary Decay in Competition – SDC; Combined Decay - CD) [25-28]. The two-body dissociation is driven by Coulomb repulsions, in which a "cigar" shape and a slope -1 are expected to the 2D ion pair projection. (C^+, O^+) and (HC^+, O^+) ion pairs (Fig. 5i and 5k, respectively) clearly show these conditions, suggesting that the charge separation process occurs. The fragmentation mechanisms could be given by:

$$CO^{2^{+}} \rightarrow C^{+} + O^{+}$$
(1)
$$HCO^{2^{+}} \rightarrow HC^{+} + O^{+}$$
(2)

In the (C^+, O^+) channel, the CS mechanism have been corroborated by the CO fragmentation [29]. The ion pairs (H^+, HCO^+) and (OH^+, HCO^+) don't show the "cigar" shape (Fig. 5h and 5n, respectively), but their dissociation processes should be driven by CS mechanisms:

$$\begin{array}{l} \text{HCOOH}^{2+} \rightarrow \text{H}^{+} + \text{HCOO}^{+} \\ \text{HCOOH}^{2+} \rightarrow \text{OH}^{+} + \text{HCO}^{+} \end{array}$$
(3)

The ion pairs (C^+,OH^+) , (O^+,CO^+) and (OH^+,CO^+) projections suggest that the three-body decay deferred charge separation (DCS) is the dissociation process in these channels. They show a "bar" shape with a slope close to -1 (Fig. 5j, 5l and 5m, respectively). The fragmentation mechanisms could be given by:

$$COOH^{2+} \rightarrow O + COH^{2+}$$
(5a)

(51.)

$$HCOO^{2+} \rightarrow H + COO^{2+}$$
(50)

$$COO^{2+} \rightarrow O^+ + CO^+ \tag{6b}$$

$$\text{HCOOH}^{2+} \rightarrow \text{H} + \text{COOH}^{2+}$$
 (7a)

$$COOH^{2+} \rightarrow OH^{+} + CO^{+} \tag{7b}$$



Figure 5 – 2D ion pair projections from PEPIPICO signals measured at 532 eV. The assignments are shown in the figure panels.

$HCO^{2+} \rightarrow H^+ + C + O^+$	(8)
$HCOOH^{2+} \rightarrow H^+ + CO + OH^+$	(10)
$HCOO^{2+} \rightarrow H^+ + O + CO^+$	(11)
$\text{HCOOH}^{2+} \rightarrow \text{H}^+ + \text{O} + \text{HCO}^+$	(12)
$HCOOH^{2+} \rightarrow H^+ + H + COO^+$	(13)

The ion pairs (H^+,C^+) and (H^+,HC^+) projections suggest that the three-body decay secondary decay (SD) is the dissociation process in these channels. They show a parallelogram shape with a slope close to -1 for the second pair (Fig. 5a and 5b, respectively). The fragmentation mechanisms could be given by:

$$HCO^{2+} \rightarrow H^{+} + CO^{+}$$
(14a)

$$CO^* \to C^* + O \tag{14b}$$

$$\begin{array}{l} \text{HCOH}^{2+} \rightarrow \text{H}^{+} + \text{HCO}^{+} & (15a) \\ \text{HCO}^{+} \rightarrow \text{HC}^{+} + \text{O} & (15b) \end{array}$$

4. SUMMARY

Multi-ion coincidences (PEPICO and PEPIPICO), partial ion yields (PIY) and their respective branching ratios (BR) spectra for the formic acid have been measured at the O 1s edge. The PIY and BR signals for all ions produced after excitation of gaseous formic acid were shown. The fragmentation dynamic of this simplest carboxylic acid was investigated and the fragmentation mechanisms of each dissociation channels were suggested.

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