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Complex fragmentation pathways of rhodanine and rhodanine-3-acetic acid upon resonant capture of low-energy electrons

Stanislav A. Pshenichnyuk[a,*], Alberto Modelli[b,c]

[a] Institute of Physics of Molecules and Crystals, Ufa Research Center, Russian Academy of Sciences, October Avenue, 151, 450075 Ufa, Russia
[b] Dipartimento di Chimica "G. Ciamician", Universitá di Bologna, via Selmi 2, 40126 Bologna, Italy
[c] Centro Interdipartimentale di Ricerca in Scienze Ambientali (CIRSA), Universitá di Bologna, via S. Alberto 163, 48123 Ravenna, Italy

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ABSTRACT

A detailed gas-phase study of dissociative electron attachment (DEA) to rhodanine (**Rd**) and its 3-acetic acid derivative (**Rdaa**) in the 0–14 eV energy range has been carried out with a magnetic mass spectrometer under conditions of medium energy resolution (0.4 eV) of the incident electron beam, and high sensitivity. The DEA spectra reveal the occurrence of numerous and complex dissociative decay channels of the molecular anions formed by resonances, involving multiple bond cleavage and structural rearrangements. Along with a variety of anion fragments normally formed in the collision cell at incident electron energies <1 eV, dissociation of a series of metastable anion species (occurring in the time scale of microseconds) is also detected. The observation of these slow processes is consistent with the complexity of many dissociative channels, and allows to propose schemes for the fragmentation pathways. The DEA spectra of both **Rd** and **Rdaa** also display small yields of molecular anions at zero energy. Their lifetimes with respect to electron detachment are experimentally evaluated to be about 30 μs and 200 μs, respectively. These (vibrationally excited) ground anion states formed by capture of thermal electrons mainly into the ring π* (C=S) LUMO survive long enough to redistribute their excess energy before undergoing different dissociation channels.

1. Introduction

The electron-acceptor rhodanine (**Rd**) derivative rhodanine-3-acetic acid (**Rdaa**, see Chart 1) was found to be a promising candidate for dye-sensitized solar cell components [1]. However, a recent electron transmission spectroscopy (ETS) [2] and dissociative electron attachment spectroscopy (DEAS) [3] study [4] showed that attachment of slow electrons to these compounds is followed by dissociation, thus casting serious doubts on their long-term stability under conditions of excess negative charge.

The aim of the present study is to get more insight into the complex dissociation channels which follow low-energy resonant electron capture in the above mentioned gas-phase molecules. This investigation was performed by means of the electron attachment spectroscopy (EAS) technique using a magnetic mass filter [5] in the 0–14 eV incident electron energy range. Setting the instrumental sensitivity as high as possible, some decay channels of the molecular anion that escaped detection in the former study [4] could be revealed. Most importantly, the present experimental equipment can reveal fragmentation pathways which involve formation of metastable anions, i.e., dissociation processes which take place in a time scale of the order of magnitude of microseconds. The structures and yields of some negative fragments could be determined taking advantage of isotopic analysis.

2. Experiment

Our EAS apparatus coupled with a negative ion mass spectrometer has been previously described [5,6]. Briefly, a magnetically collimated electron beam is passed through a collision cell filled with a gas of the substance under investigation. A current of mass-selected negative ions formed inside the collision cell by resonant electron attachment is recorded as a function of the incident electron energy. The accessible electron energy range is 0–14 eV, and the electron beam saturation current is 1 μA. The electron energy scale is calibrated with the SF_6^- signal at zero energy under attachment of thermal electrons to SF_6. The full width at half-maximum of the electron energy distribution is estimated to be 0.3–0.4 eV, and the accuracy of the measured peak energies ±0.1 eV.

Evaluation of the electron detachment time is based on detection of the neutral species formed by electron detachment from negative ions during their flight through the field-free region between the mass analyzer and the secondary electron multiplier. This method, previously proposed [7] for time-of-flight experi-

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* Corresponding author.
E-mail address: sapsh@anrb.ru (S.A. Pshenichnyuk).

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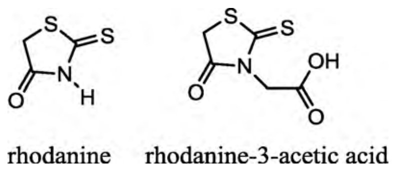

Chart 1.

ments, can be modified for magnetic mass spectrometers [5]. In the present experimental equipment the lifetimes required for detection through the mass filter are about 26 μs and 29 μs for the **Rd** and **Rdaa** molecular anions, respectively.

A sufficient sample pressure in the collision cell, under single-collision conditions, was obtained heating **Rd** ($C_3H_3NOS_2$) and **Rdaa** ($C_5H_5NO_3S_2$) at 80 and 90 °C, respectively. The temperature of the walls of the collision cell was kept at 90 °C in both cases. The samples are commercially available (Aldrich).

Geometry optimizations and evaluation of total energies were performed with the Gaussian 03 set of programs [8], using the B3LYP hybrid functional [9] with the standard 6−31+G(d) basis set.

3. Results

3.1. Negative ions formed by resonant electron capture

3.1.1. Rhodanine

Fig. 1 shows the most intense anion currents generated by electron attachment to gas-phase **Rd**. The results are in good agreement with an earlier DEA investigation [4] carried out using an apparatus with a higher energy resolution of the incident electron beam, but a smaller sensitivity. The measured peak energies and relative intensities are listed in Table 1. The most intense current ($m/e = 91$, peaking at 0.6 eV) is due to loss of a ketene (H_2CCO) molecule. The peak at 0.9 eV in the yield of the **Rd** molecular anion ($m/e = 133$) is entirely (intensity and shape) accounted for by isotopic contributions (about 5.4%) from the more intense $m/e = 132$ dehydrogenated anion, peaking at the same energy.

Many other negative fragments generated by dissociation of the parent anion of **Rd** were detected. Their intensities are smaller than that of the $m/e = 91$ anion fragment by several orders of magnitude (see Table 1). Currents of these negative ions, as a function of the

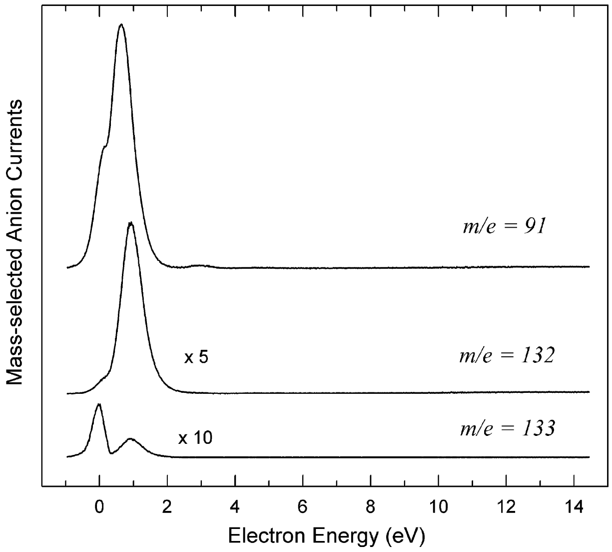

Fig. 1. Most intense mass-selected anion currents, as a function of the incident electron energy, formed by DEA to gas-phase **Rd**.

Table 1
Peak energies (eV) and relative intensities (evaluated from the peak heights) of the anion currents measured in the DEA spectrum of rhodanine (**Rd**) at 90 °C.

m/e	Anion structure	Peak energy (eV)	Relative intensity
26	$[CN]^-$	0.0	<0.1
		1.7	<0.1
		3.2	0.13
		4.5	0.15
		9.2	<0.1
32	$[S]^-$	0.2	<0.1
		3.2	0.16
		4.5	0.31
		6.3 sh.	
33	$[SH]^-$	0.0	0.10
		1.8 sh.	
		3.2	<0.1
		4.5	0.10
37.0	m_1^*: 91 → 58	0.0 sh.	
		0.6	<0.1
		3.0	<0.1
40	$[CCO]^-$	3.0	<0.1
		4.4	<0.1
41	$[CHCO]^-$	3.4	<0.1
		4.4	0.10
42	$[OCN]^-$	3.2	0.23
		4.5	0.51
45	$[SCH]^-$	0.6	<0.1
		4–6 broad	<0.1
		8.1	<0.1
46	$[CH_2S]^-$	0.0	<0.1
		3.1	0.29
		4.4	0.51
57	$[Rd–CS_2]^-$	1.3	<0.1
		3.1	0.31
		4.4 sh.	
58	$[SCN]^-$	0.0 sh.	
		0.6	0.42
		3.1	2.55
		4.4	3.01
60	$[OCS]^-$	3.1	0.10
		4.3	0.10
62.3	m_2^*: 133 → 91	0.0	<0.1
		0.7	<0.1
64	$[S_2]^-$	0.0	<0.1
		3.1	<0.1
		4.5	0.10
72	$[SCCO]^-$	0.0	<0.1
		1.2	<0.1
		3.0	0.11
		4.4	0.10
73	$[Rd–OCS]^-$	3.2	0.10
		4.6	0.14
		7.9	<0.1
74	$[SCH_2CO]^-$	0.0	<0.1
		1.0	<0.1
		3.0	<0.1
		4.5	<0.1
75	[Rd–SCN]-	0.0	0.10
		0.6 sh.	
76	$[CS_2]^-$	0.9	<0.1
		3.2 sh.	
		4.5	<0.1
		6.3 sh.	
91	$[Rd–H_2CCO]^-$	0.0 sh.	
		0.6	100
		3.0	1.00
100	$[Rd–SH]^-$	0.7	<0.1
		3.0	0.18
105	$[Rd–CO]^-$	0.0 sh.	
		1.0	0.27
132	$[Rd–H]^-$	0.0 sh.	
		0.9	13.9
133	$[Rd]^-$, 30 μs	0.0	2.14