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Negative ion mass spectra of some phenalenone derivatives

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ABSTRACT

Temperature dependence of the negative ion mass spectra (NIMS) of six phenalenone derivatives has been investigated using a mass spectrometer with the static magnetic field mass analyzer. The dissociative attachment cross-section and the mean lifetime of the molecular NI's decreases approximately exponentially with the temperature rising, and the dissociative attachment cross-section of fragment ions generally increases with temperature. The mean lifetime of the molecular anions is at least tens of microseconds for all the investigated compounds.

1. Introduction

Some organic compounds, e.g. nitrobenzene [1] and anthraquinone derivatives [2], may produce long-lived molecular negative ions (MNI) having a dissociation decay channel at low electron energies. Their NIMS have peaks at the molecular mass what proves that the dissociation proceeds on a time scale comparable with the time of flight through a mass spectrometer—tens of microseconds. The mechanism of this phenomenon is not yet fully understood what motivated our search for compounds producing metastable MNIs. Phenalenone derivatives are widely distributed in nature [3,4]. Some of them exhibit antibiotic activity [5]. They are studied as environmental contaminants, as coal hydrogenation byproducts, as precursors to fullerenes [6], and as monomers for the synthesis of electroconductive polymers. Halogen-substituted phenalenone derivatives are used as laser dyes.

When a molecule captures an electron the resulting anion has an excess energy which is equal to the electron affinity plus the impinging electron energy plus the initial vibrational energy of the molecule [7,8]. Statistically, this last value is proportional to the gas temperature [9]. If the anion initially survives a time of order a molecular vibration period, the excess energy may be redistributed among internal degrees of freedom of the ion. For large molecules, the number of degrees of freedom allows thermodynamical description, and the resulting ion state may be characterized by an effective temperature [9,10].

The further evolution of the ion may proceed through the autodetachment of the electron and/or the dissociation:

$$M^{-*} \xrightarrow{k_a} M + e^-,$$

$$M^{-*} \xrightarrow{k_d} [M - R] + R^-,$$

here M stands for the molecule, and R for an appropriate fragment. Under the above conditions, one can expect that the ion's life time is long enough, and the rate constants, k_a and k_d, have an Arrhenius-type behavior with the ion temperature. It should be noted, however, that the calculation of this temperature is, generally, a very complicated problem [9,10]. Nevertheless, within this framework many useful conclusions may be made even on a qualitative level.

A negative ion mass spectrometer has an observation window of tens of microseconds. For sufficiently long-lived ions, a data gathered in a single experiment contains enough information to estimate different rate constants even when competing reaction channels are present. Analysis of dependence of these values on the target gas temperature makes possible to conclude on the validity of the above model and assess a possible contribution of repulsive electronic terms to the ion dynamics.

Phenalenone derivatives are large aromatic molecules with a positive electron affinity which makes them promising objects for this kind of study. To our best knowledge, these compounds have not yet been investigated by means of the NIMS.

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Table 1
NI mass spectra of phenalenone derivatives

m/z	E_{max} (eV)	Relative intensity	Intensity (%)	Integral intensity	Lifetime (μs)	Structure
2,6-Br_2-phenalenone. Ion source temperature 110 °C. EA_a = 1.539 eV						
338	0.14	262	100	9125	~1000 (0.0)	M^-
					720 (0.14 eV)	
79	0.5	120	45.8	6514		Br^-
	~2.1	12	4.6			
	~3	8	3.05			
m^* = 18.46	~0.3	0.3	0.11	13.27		$M^- \to Br^-$
M^0	~0.33	3.7	1.4	163		$M^- \to M^0 + e^-$
2,6-Br_2-phenalenone. Ion source temperature 140 °C						
338	0.14	165	100	5376	~800 (0.0)	M^-
					560 (0.14 eV)	
79	0.46	110	66.7	6202		Br^-
	~2.1	12	7.3			
	~3	8	4.8			
m^* = 18.46				12.66		$M^- \to Br^-$
M^0	~0.3	3.4	2.1	127		$M^- \to M^0 + e^-$
2,6-Br_2-phenalenone. Ion source temperature 170 °C						
338	0.11	135	94.4	4061	550 (0.0)	M^-
					390 (0.14 eV)	
79	0.37	143	100	7829		Br^-
	~2.1	12	8.4			
	~3	8	5.6			
m^* = 18.46				12.65		$M^- \to Br^-$
M^0	~0.22	3.4	2.4	124		$M^- \to M^0 + e^-$
2,6-Br_2-phenalenone. Ion source temperature 200 °C						
338	0.11	100	54.6	3214	~400 (0.0)	M^-
					290 (0.14 eV)	
79	0.28	183	100	9773		Br^-
	~2.1	12	6.6			
	~3	8	4.4			
m^* = 18.46				12.19		$M^- \to Br^-$
M^0	~0.15	3.2	1.7	115		$M^- \to M^0 + e^-$
m/z	E_{max} (eV)	Relative intensity	Intensity (%)	Integral intensity	Lifetime (μs)	Structure
2-Br-phenalenone. Ion source temperature 90 °C. EA_a = 1.307 eV						
258	0.22	71	49	2431	355 (0.0)	M^-
					220 (0.22 eV)	
79	0.52	145	100	7965		Br^-
	~3	17	11.7			
m^* = 24.19	~0.35	0.4	0.28	14.61		$M^- \to Br^-$
M^0	~0.34	2.57	1.8	89.89		$M^- \to M^0 + e^-$
2-Br-phenalenone. Ion source temperature 110 °C						
258	0.19	51	42.9	1717	320 (0.0)	M^-
					235 (0.22 eV)	
79	0.48	119	100	6791		Br^-
	~3	17	14.3			
m^* = 24.19	~0.35	0.23	0.19	8.93		$M^- \to Br^-$
M^0	~0.34	1.92	1.6	64.17		$M^- \to M^0 + e^-$
2-Br-phenalenone. Ion source temperature 170 °C						
258	0.16	32	19.2	966	230 (0.0)	M^-
					160 (0.22 eV)	
79	0.38	167	100	9333		Br^-
	~3	17	10.2			
m^* = 24.19	~0.36	0.22	0.13	10.97		$M^- \to Br^-$
M^0	~0.23	1.35	0.81	44.67		$M^- \to M^0 + e^-$
2-Br-phenalenone. Ion source temperature 200 °C						
258	0.14	20	8.8	579	160 (0.0)	M^-
					110 (0.22 eV)	
79	0.33	227	100	12134		Br^-
	~3	17	7.5			
m^* = 24.19	~0.25	0.19	0.08	7.60		$M^- \to Br^-$
M^0	~0.18	1.13	0.5	34.46		$M^- \to M^0 + e^-$
m/z	E_{max} (eV)	Relative intensity	Intensity (%)	Integral intensity	Lifetime (μs)	Structure
2-NO_2-phenalenone. Ion source temperature 110 °C. EA_a = 1.818 eV						
225	0.01	1176	100	68802	~50000 (0.0)	M^-
	0.34	1157	98.4		15700 (0.34 eV)	
195	2.14	16.8	1.4	1599		$(M\text{-}NO)^-$
46	2.33	371	31.5	60692		NO_2^-