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Received April 13, 1999

## Mass spectra of the negative ions of some dioxanes

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It was established by mass spectrometry of negative ions that fragmentation of some 1,3- and 1,4-dioxanes proceeds through intermediate  $[M - H]^-$  ions. The fragmentation pathway depends on the site of negative charge localization in these ions.

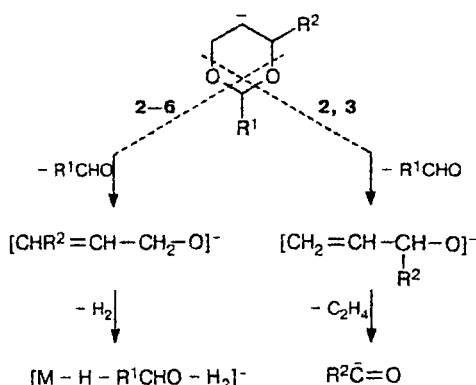
**Key words:** substituted dioxanes, resonance capture of electrons, negative ions, mass spectra, fragmentation,  $[M - H]^-$  ions.

Earlier,<sup>1</sup> we studied the formation of negative ions (NIs) from molecules of 1,3-dithianes and 1,3-dithiolanes using mass spectrometry of NIs in the regime of resonance capture of electrons. The present paper reports the results of a study of the formation of NIs from molecules of 1,4-dioxane (1), 1,3-dioxane (2), 2-methyl-1,3-dioxane (3), 2-phenyl-1,3-dioxane (4), 4-phenyl-1,3-dioxane (5), 2-vinyl-1,3-dioxane (6), and 2-nitrophenyl-1,3-dioxane (7).

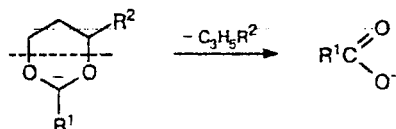
Compounds 1–6 form NIs by capturing electrons with energies –8–9 and 6–7 eV, the latter providing lower yields (Table 1). These resonances are difficult to interpret because the photoelectronic spectra contain little information. Even in the case of compounds 1 and 2, i.e., the simplest dioxanes, we could determine (because of broad ionization bands) only the ionization energies corresponding to removal of an electron from combinations of lone electron pairs on oxygen atoms,  $n^-_O$  and  $n^+_O$ .<sup>2</sup> Nevertheless, one can state that compounds 1–6 form NIs in the region of electron-excited molecular states.

The fragmentation of compounds 2, 4, and 5 mainly proceeds through  $[M - 31]^-$  ions presumably formed upon loss of a formaldehyde molecule from  $[M - H]^-$  ions.

An analysis of the mass spectra of compounds 2–6 shows that the fragmentation can be represented by a scheme of decomposition of  $[M - H]^-$  ions with charge localization on the C(5) atom (this scheme requires minimum structural changes).

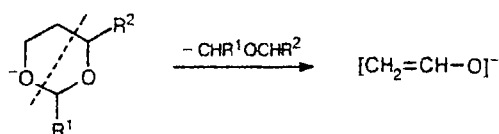


Another pathway of the fragmentation of 1,3-dioxane, which leads to NIs with  $m/z$  45 ( $C_2H_5O^-$ ), is less distinct and implies removal of a hydrogen atom from the C(2) atom:



When  $R^1 = Ph$ , this pathway becomes more pronounced, probably, because of a greater stability of both the resulting ion and NI  $[M - H]^-$  with charge localization on the C(2) atom.

tion on the C(2) atom. These data correlate with the high C—H acidity of the hydrogen atom in position 2 in 1,3-dioxane.<sup>3</sup> Hence, interpretation of the pathways of fragmentation of molecular NIs related to charge localization on the C(5) atom seems, at first glance, unjustified. However, it was shown<sup>4</sup> by the method of ion-cyclotron resonance with the use of labeled compounds that in the gaseous phase the hydrogen atom is predominantly removed from the C(5) atom rather than from the other positions. This conclusion finds support in the presence of peaks from ions with  $m/z$  43 in the mass spectra of compounds 2–6, whose formation may be explained by the fragmentation of the  $[M - H]^-$  ion with charge localization on the C(4) or C(6) atoms:



Thus, the fragmentation of molecular NIs of 1,3-dioxanes 2–6 may be largely related to the structure of intermediate  $[M - H]^-$  ions, though the latter are observed only for phenyl-substituted compounds 4 and 5. The absence of  $[M - H]^-$  ions in the mass spectra of compounds 2, 3, and 6 is probably associated with their instability; they undergo fragmentation involving thermodynamically favorable elimination of a  $CH_2=O$  molecule. Note that, in the case of 1,3-dithiane, the barrier to the elimination of a  $CH_2=S$  molecule from  $[M - H]^-$  ions with charge localization on the C(5) atom amounts to 20.5 kcal mol<sup>-1</sup>.<sup>4</sup> Insofar as a  $CH_2=O$  molecule eliminated from the NI of 1,3-dioxane is more stable (by nearly the same value) than  $CH_2=S$ , it is not surprising that no  $[M - H]^-$  ions are observed in the mass spectra of compounds 1–3 and 6.

The mechanism of formation of NIs sharply changes when passing to compound 7, in which the nitrophenyl fragment can effectively capture an electron. The mass spectrum of 7 shows an intense peak of the molecular

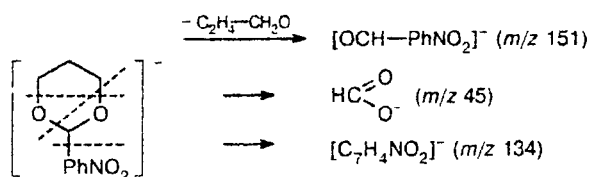
**Table 1.** Mass spectra of the negative ions of substituted dioxanes

Compound	Molecular weight	$m/z$	$I_{rel}$ (%)	$E/eV$
(1)	88	43	100	7.6
			55	~9.3
		41	1.8	7.7
			2.4	10.0
(2)	88	57	100	8.3
		55	~3	8.4
			3.5	9.1
		45	4	7.3
			4	8.3
			4	9.0
			3	10.6
		43	4	8.5
		29	0.7	7.3
			4	9.0
			0.6	10.6
(3)	102	57	58	8.3
		43	100	8.6
			25	~10.0
		41	14	6.4
			15	8.7
			15	10.0
		29	2	9.0
		15	8	6.4
(4)	164	163	1.5	5.9
			16	8.0
		133	10	6.0
			0.7	8.1
		121	54	6.4
			5	8.1
		107	12	6.7
(5)	164		10	7.7
		105	4	6.8
			9	8.2
		77	19	6.0
			18	8.0
		57	15	6.4
			100	7.7
		43	5	8.2
(6)	114	163	7.5	6.1
			46	8.3
		133	95	8.4
		131	28	8.8
		103	100	8.5
		77	43	8.9
		55	45	9.0
(6)	114	43	2	8.4
		71	9	6.7
			2.5	8.4
		57	100	8.4
		55	4	~6.8
			35	8.6
		43	9	6.8
			9	8.4
			9	9.6

Note:  $I_{rel}$  is the intensity of ion peaks<sup>5</sup>;  $E$  is the maximum energy of electrons on the curve of effective formation of ions (the formation of  $O^-$  and  $OH^-$  ions were observed for all compounds, but their intensities could not be determined reliably because of a strong background signal and are not cited in the mass spectra); the relative cross sections ( $Q$ ) giving ions with maximum peaks (they were compared with the cross section producing  $C_6H_5^-$  from benzene and taken<sup>6</sup> to be equal to  $8 \cdot 10^{-20}$  cm<sup>2</sup>):  $Q \cdot 10^{20}/\text{cm}^2 = 32$  (1), 14 (2), and 9.5 (3).

NI (its average lifetime with respect to the electron autodetachment  $\tau_a = 83 \mu\text{s}$ ) in the range of electron thermal energy. This value is almost twice as high as that for nitrobenzene<sup>7</sup> ( $\tau = 48 \mu\text{s}$ ), which indicates that the 1,3-dioxane fragment stabilizes the molecular NI of compound 7.

The main fragmentation processes in the molecular NIs of compound 7 involve the decomposition of the dioxane ring and are due to charge localization on the nitrophenyl fragment.



In addition, unlike the other compounds under study, the mass spectrum of the NI of compound 7 exhibits no resonances in the range of electron energy of 8–9 eV. Apparently, this is caused by the fact that the number of resonances related to electron transitions to high-energy unoccupied MOs of the 1,3-dioxane fragment decreases because of the presence of low-energy unoccupied MOs with the major contributions from the nitrophenyl fragment. Nevertheless, the 1,3-dioxane fragment slightly stabilizes the resonances (by  $\sim 0.2$ – $0.3$  eV) as compared to nitrobenzene.

### Experimental

Mass spectra of the NIs of dioxanes 1–7 were obtained with an MI-1201 mass spectrometer modified for registering NIs.<sup>5</sup> An electron energy scale was calibrated using the maxima

on the curves of effective formation of  $\text{SF}_6^-$  from  $\text{SF}_6$  (0 eV) and  $\text{NH}_2^-$  from  $\text{NH}_3$  (5.65 eV). 1,4-Dioxane (Aldrich) was used. Compounds 2–6 were prepared according to the known procedure.<sup>8</sup>

The mass spectrum of the NI of 2-(4-nitrophenyl)-1,3-dioxane 7 ( $m/z$ , ion composition,  $I_{\text{rel}}$  (%), resonance maximum energy, eV (given in parentheses)): 209  $[\text{M}]^-$ , 75.8 (0.1); 151  $[\text{NO}_2\text{C}_6\text{H}_4\text{CHO}]^-$ , 35.6 (0); 134  $[\text{NOC}_6\text{H}_4\text{CO}]^-$ , 0.45 (3.9); 121  $[\text{C}_6\text{H}_4\text{CHO}_2]^-$ , 8.9 (0.3), 0.4 (4.05); 106  $[\text{NOC}_6\text{H}_4]^-$ , 0.2 (4); 105  $[\text{C}_6\text{H}_4\text{CHO}]^-$ , 0.2 (4.1); 93  $[\text{C}_6\text{H}_4\text{OH}]^-$ , 0.4 (1), 0.6 (4.6); 92, 0.1 (4.3); 91, 0.2 (4); 89, 0.04 (4.1); 79, 0.1 (4.1); 78, 0.1 (4.1), 0.03 ( $\sim 6.7$ ); 46  $[\text{NO}_2]^-$ , 100 (0.8), 41.7 (3.7); 45, 0.2 (0.15), 0.2 (3.9); 43, 0.2 (4); 42, 0.15 (4.1); 26  $[\text{CN}]^-$ , 0.8 (4); 17  $[\text{OH}]^-$  (0.2), 0.08 ( $\sim 6.7$ ); 16  $[\text{O}]^-$ , 0.8 (4.6).

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Received April 13, 1999