



Negative ion mass spectrum of the resonance electron capture by molecules of *p*-benzoquinone

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ABSTRACT

The negative ion mass spectrum of the resonant electron capture by molecules of *p*-benzoquinone has been recorded. It has been found that apart from the well-known earlier five types of negative fragmental and long-lived molecular ions, 17 more types of other fragmental ions are produced in this compound. The scheme of the molecular ion decay has been composed for each dissociation channel, where the choice has been given to the structures of the dissociation products which in accordance with MNDO calculations have the minimal total energies. The effective yield curves of the negative ions have been recorded as functions of the electron energy. It has been also assumed that the long-lived negative molecular ions of *p*-benzoquinone are formed, probably, in two resonant states close in energy and poorly resolved: at 1.36 and 1.56 eV.

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1. Introduction

p-Benzoquinone (PBQ) is intensively studied for a number of years as a key compound among quinones. The quinones, in their turn, present much interest because they have a variety of unique properties that provide their participation in many important processes, such as electron transfer at photosynthesis [1–3]. Many of unusual properties of the quinones depend upon features of the electron capture by their molecules. However, the laws operating these processes are still far from being absolutely clear. It mainly concerns the well-known ability of the quinone molecule, including PBQ, to capture an additional electron with the kinetic energy (E_{el}) considerably exceeding the zero, and to keep it for a long time, being in gas phase under the conditions of single collisions. This phenomenon has been discovered for the first time in the work [4] using the example of PBQ that has been later confirmed in subsequent studies [5,6]. In particular, in the work [6], it has been obtained that PBQ negative molecular ions (M^-) are produced at $E_{el} = 1.35$ eV and their average lifetime regarding the electron autodetachment (τ) account for $\tau \approx 3 \times 10^{-5}$ s. In this case, such τ value is abnormally high because under these conditions the M^- ion cannot dissipate the energy excess obtained with an additional electron. The ion remains in energy above the

parent molecule of the ground electronic state ($^GSM^0$) by the E_{el} value during the whole time of the existence, and this should lead rapidly (in 10^{-14} to 10^{-15} s) to autodetachment of the additional electron with the same E_{el} which it was captured with by the molecule. But, in the quinones, this does not occur. Recently, some of the authors of the present work have shown that this anomaly is caused by transformation of the ‘initial’ molecular ion-doublet ($^DM^-$) formed directly at the electron capture by molecule into an ion-quartet ($^QM^-$) having three unpaired electrons with parallel spins [7,8]. The transformation is a result of nonradiative transition of the system from the $^DM^-$ potential energy surface onto the $^QM^-$ ion surface with spin flip of one of the electrons at the surfaces intersection point, and the high $^QM^-$ τ value is explained by the necessity of the similar spin flip at the $^QM^- \rightarrow ^GSM^0$ transition. This result can be applicable to gain a better understanding of both the electron–molecular interactions in general and the molecular mechanisms providing the important quinones properties in particular. However, to achieve this objective the concept should be developed further, that assumes, among other things, one more experimental study of PBQ in addition to those, which have been carried out by other authors earlier. In this connection, the negative ion mass spectrum (NIMS) of the resonant electron capture by PBQ molecules was obtained in the present work, with registration of all fragmental negative ions (FNIs), including low-intensive ones, and with recording of the corresponding effective yield curves (EYCs) as functions of the incident electron energy E_{el} . These data can be useful in solving various problems,

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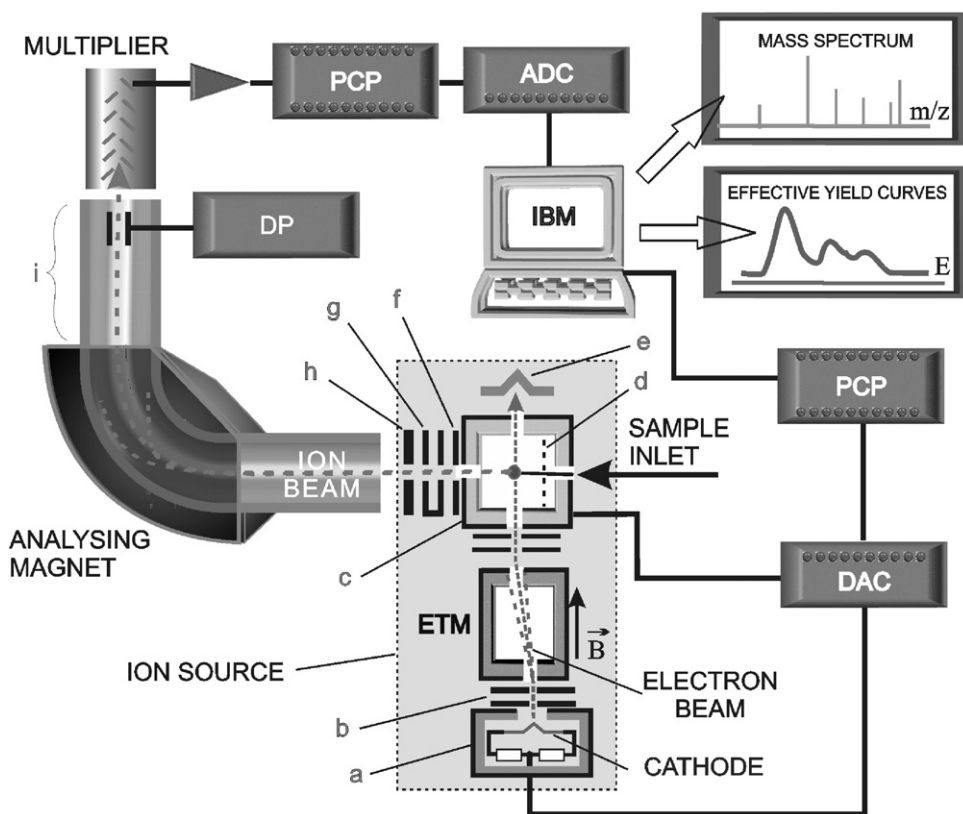


Fig. 1. Block-scheme of static magnetic sector mass spectrometer modified for registration of negative ions in resonant electron capture regime. Cathode chamber (a); electron extracting lenses (b); ionization chamber (c); repeller (d); electron collector (e); ion extracting lens (f); ion focusing lens (g); ion accelerating lens (h); drift space (i). Deflecting plates (DP); photon-coupled pair (PCP); analog-to-digital converter (ADC); digital-to-analog converter (DAC).

for instance, when determining one of the essential characteristics of the intercombination conversion, namely, the electronic configuration of the M^- ion transformed in the course of this process.

2. Experimental/materials and methods

The NI mass spectrum of the resonant electron capture of PBQ was recorded using a MI-1201B static magnetic sector mass spectrometer (JSC Selmi, Ukraine), modified for registration of the negative ions in the regime of the resonant electron capture [9] (Fig. 1).¹ The instrument operates as follows.

Monoenergetic electrons and negative ions are formed in the ion source (the shaded rectangle in Fig. 1). At first, the electrons are emitted from the heated tungsten cathode placed into the cathode chamber 'a', then they go through two extracting diaphragms-lenses 'b', which have a minor positive potential, and then come into the ionization chamber 'c'. They enter the chamber 'c' in two possible ways, depending on the experimental task: through the electronic trochoidal monochromator (ETM), constructed according to [11], or directly, when ETM is absent. In the last case, focusing of the electrons is provided by a special magnet (not shown in Fig. 1). But in both cases, the electrons are accelerated up to the desired energy (within the 0–15 eV) by variations of the potential difference between the cathode middle point and the ionization chamber box. These variations are carried out by means of a computer-controlled digital-to-analog converter (DAC). The sys-

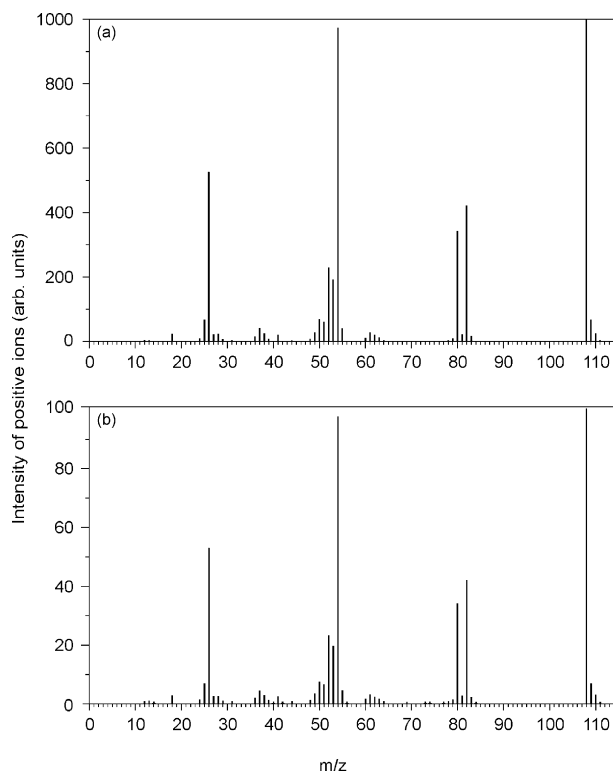


Fig. 2. *p*-Benzoquinone positive ion mass spectrum from present work (a) and from data base [14] (b).

¹ The picture with some changes was taken from [10] with author's permission.

tem with ETM creates distribution of the electron energy of 0.1 eV (defined by the half-height of the EYC of SF_6^-) at the electron current of 0.1 μA . Since this current is rather low, such system is used, as a rule, for registration of intensive ions. In the present work, the M^- ions of PBQ were recorded with ETM. When ETM is absent, the system gives the distribution of 0.3–0.4 eV at the current of 1 μA , and due to the higher value of the current it can be used for investigation of low-intensive ions. In the present work all FNIs of PBQ were recorded by means of this construction (without ETM).

The negative ions are generated in the ionization chamber 'c' (Fig. 1). The formed ions are extracted from the chamber 'c' by the positive potential of the lens 'f', focused by the lens 'g' and accelerated to the magnet-analyzer by the lens 'h' which is the exit slit of the ion source. The ion acceleration occurs on the path from the lens 'g' to the lens 'h', which is achieved by a high negative potential (up to -4 kV) applied on the ion source as whole, except the lens 'h', whereas, the lens 'h' is kept under the ground potential.

Further, the ions enter into the analyzer tube, go through it and get registered by the secondary electron multiplier, the last dynode of which is kept under the high positive potential of 2–3 kV. The multiplier signal is transmitted at first to the photon-coupled pair (PTP), which uncouples high and low potentials, then to the analogue-to-digital converter (ADC) and, at last, to the computer, which is kept under the ground potential. The computer records the ion signal of the given m/z as a function of the electron energy after several cycles of the digital accumulation. This provides the EYCs. Apart from that, it registers also the NI mass spectrum as such.

In the present work, the τ value was estimated on the basis of the exponential law of the M^- ions decay caused by electron autodetachment [12,13]. The law is written as $N_S = N_0 e^{-t/\tau}$, where N_S is the number of the ions which have survived through time t , N_0 is the initial number of ions, and τ is their average lifetime. The t value is known to be equal to 6 μs , as a characteristic of our mass spectrometer. The N_S/N_0 relation can be estimated experi-

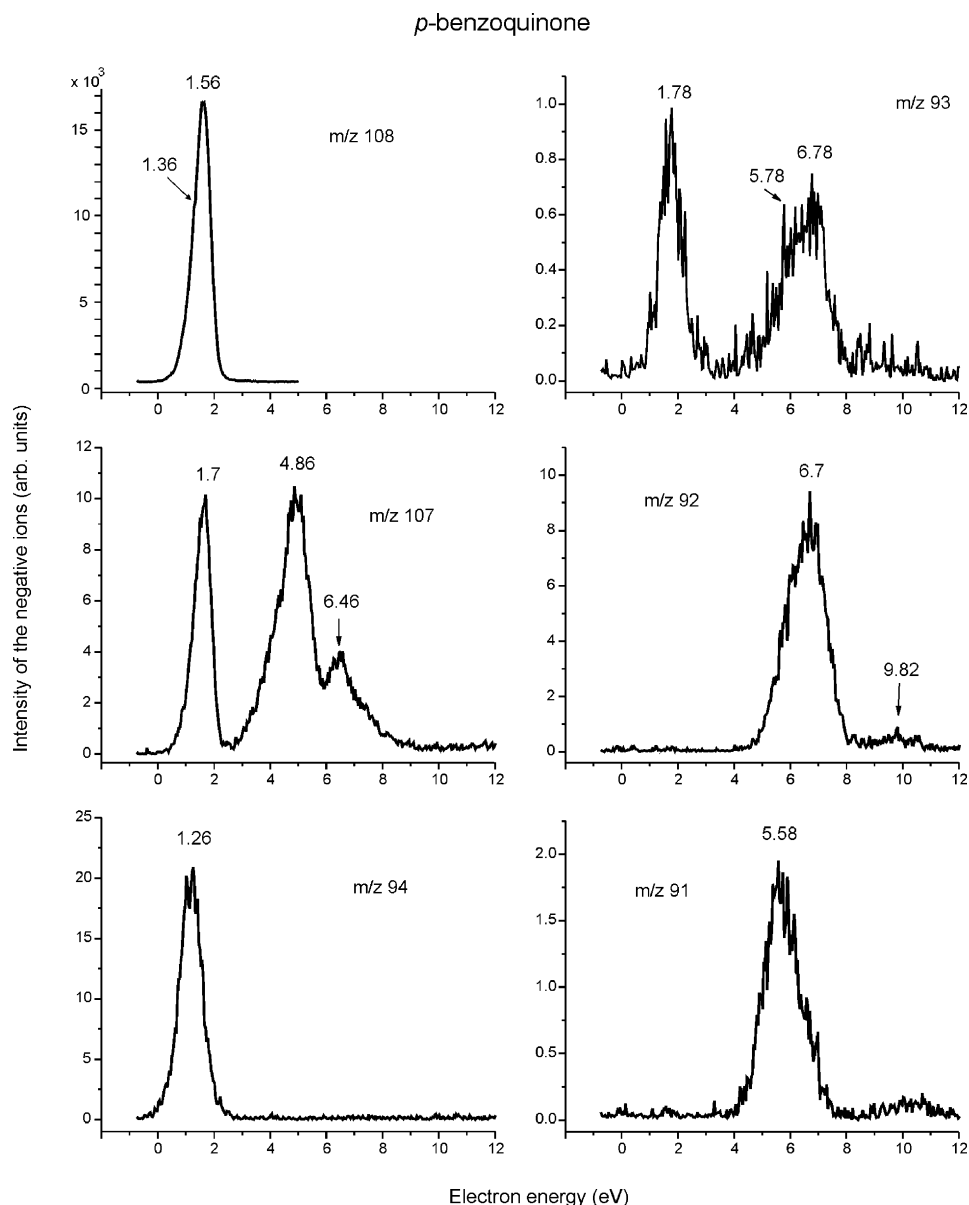


Fig. 3. Effective yield curves for negative ions with m/z 108, 107 and 94–91.

mentally using deflecting plates ('DP' in Fig. 1) placed before the multiplier collector. When the plates have no a potential, the multiplier registers a common current (I_{com}) of the ions and neutrals, where the neutrals are the molecules generated as a result of the M^- ions part decay. This decay occurs in the drift space between the analyzer and the first dynode of the multiplier (the length ' l ' in Fig. 1), through the electron autodetachment. The I_{com} current corresponds to the N_0 number. When a potential on the plates is applied, the ion component is removed from the common beam. In this case, only neutral component is registered (I_{neu}). The difference of two currents ($I_{\text{com}} - I_{\text{neu}}$) corresponds to the N_S value. Therefore, $N_S/N_0 = (I_{\text{com}} - I_{\text{neu}})/I_{\text{com}}$, which allows (with $t = 6 \mu\text{s}$) to establish the τ value by means of the above-stated equation: $N_S = N_0 e^{-t/\tau}$.

The electron energy (E_{el}) was varied, during the experiment, within the 0–12 eV. The scale of E_{el} values was calibrated by the maxima of EYC for SF_6^- (0 eV) and C_6H_5^- (8.0 eV) ions from SF_6 and C_6H_6 , respectively. The temperature of the ionization chamber was of $\approx 55^\circ\text{C}$, the pressure was no higher than $P = 10^{-4}$ Pa. As

the single collisions conditions are broken only at $P \sim 10^{-3}$ Pa, secondary processes including ion stabilization by collisions did not take place in the course of the experiment. The sample of the compound under investigation was provided by Prof. F. Galin (Institute of Organic Chemistry, Ufa Research Centre of Russian Academy of Sciences).

3. Results

In order to verify the purity of PBQ sample under study, its positive ion mass spectrum (PIMS) was recorded at 70 eV (Fig. 2a) on the same mass spectrometer that was used for the NIMS recording, but switched over to operation in the standard regime. Besides, the analogous standard PIMS of PBQ was taken from the database [14] (Fig. 2b). Comparison of these two mass spectra showed that they were identical. It should also be noted, that any ions with higher m/z values, than 108 (i.e., higher than the molecular ion), with exception of the isotope peaks of m/z 109.02112 (6.63%); m/z 110.02112 (0.60%), etc., were not observed in our PIMS. Apart from

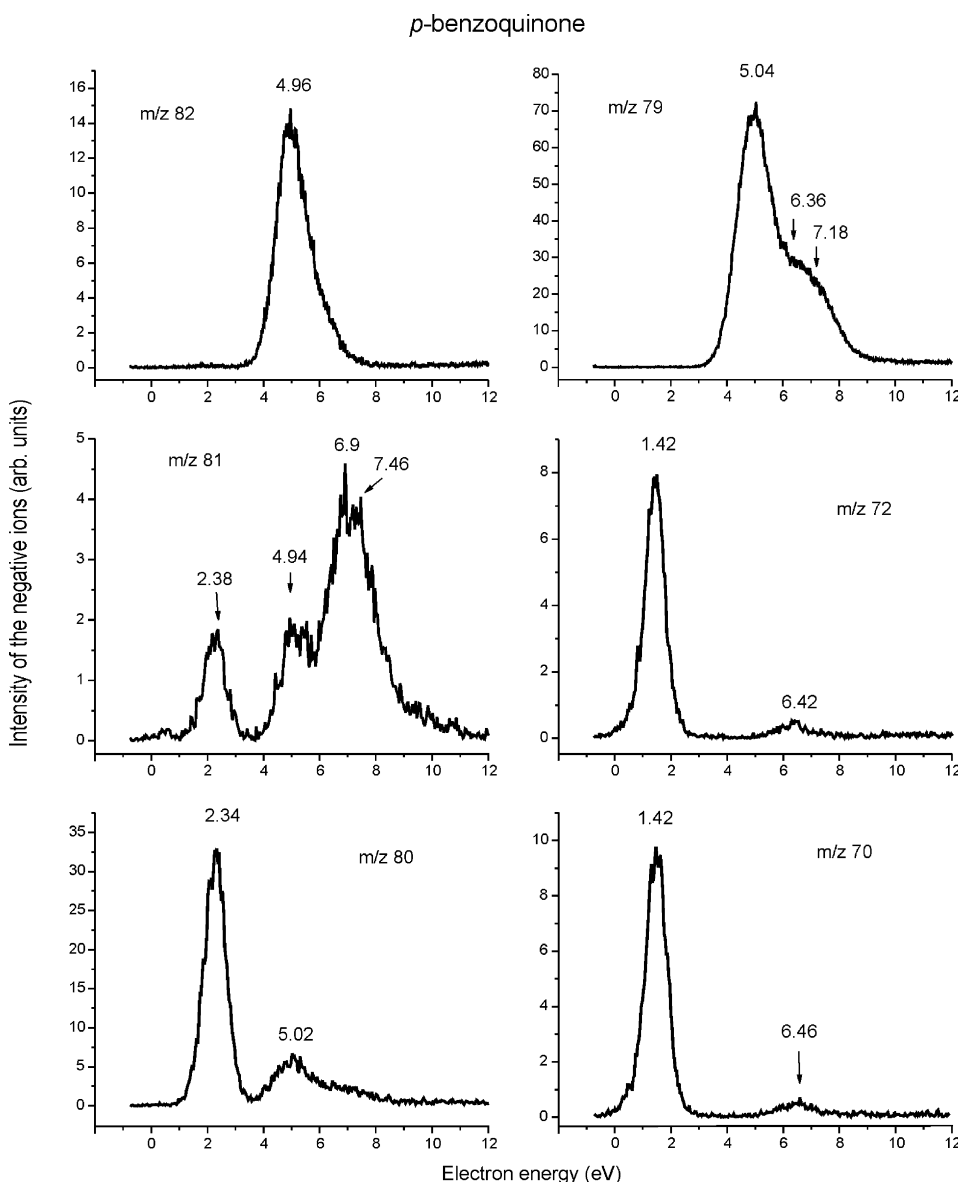


Fig. 4. Effective yield curves for negative ions with m/z 82–79, 72 and 70.

that the absence of foreign processes capable to produce pseudo-FNIs was also checked. Decomposition of the substance on the cathode could be such process. But in that case, the disproportionate changes of the relative intensities of some negative ions could be observed with changes of the cathode heating, which were not detected. The influence of the instrument background was also excluded.

PBQ NIMS obtained in the present work is given in Table 1, where one can see that this spectrum is comprised of anions of 24 types, one of which represents the M^- (m/z 108) ions having 100% intensity, and the others are the various FNIs. The maxima energies of all corresponding EYC are presented in the right column of Table 1. Like the earlier results [4–6], the EYC maximum of the M^- ions is registered at $E_{el} > 0$. But in our case this maximum is placed at $E_{el} = 1.56$ eV, which differs from data of Ref. [6] by 0.21 eV. The possible causes of this disagreement are discussed below. As regards FNIs, five types of the most intensive of them (m/z 82, 80, 79, 41 and 25) are well known from Ref. [6]. They are marked by bold type in Table 1 along with the M^- ions. The other FNIs were revealed in

the present work for the first time. EYC of all negative ions formed in PBQ are shown in Figs. 3–6.

4. Discussion

The schemes of the M^- ion decomposition pathways were constructed for all FNIs of the PBQ spectrum, of both revealed for the first time and known earlier (Figs. 7–10). At creation of the schemes, there was often a problem when different gross-formulae or different isomers of the dissociation products corresponded to the given m/z value. In these cases the choice was given to the structures, which are characterized by the minimal total energy (E_t) according to MNDO calculations. For example, m/z 92 corresponds to both structures $[C_6OH_4]^-$ (emission of atom O from the M^- ion) and $[C_5O_2]^-$ (emission of methane molecule). The second variant was assumed here (Fig. 7, Table 1) because the summarized E_t value of both dissociation products in this (second) case is lower than in the first one by 5 eV. The neutral fragment of this (second) case has also two possible structures: $[CH_2 + H_2]$ and methane

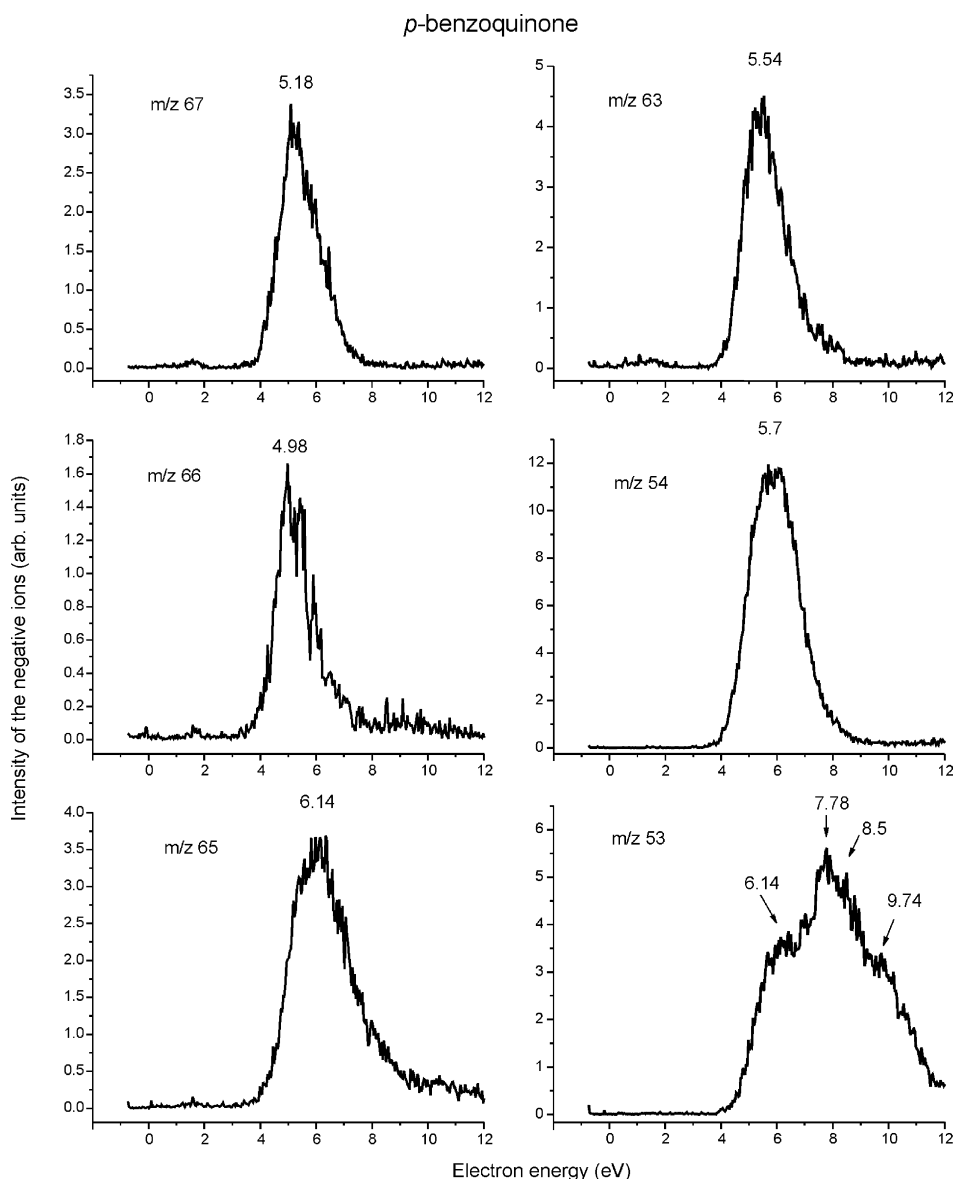


Fig. 5. Effective yield curves for negative ions with m/z 67–65, 63, 54 and 53.

molecule. The latter was chosen here again as a structure with a minimal E_t . In general, the schemes indicate that all detected ions gross-formulae correspond to the atomic composition of PBQ molecule.

The schemes allow also to conclude that the formation of all FNIs of PBQ, including revealed for the first time, corresponds to the well-known rules [15]. One of them is a rule of the 'direct bond breakage', which specifies the essential rearrangements of the M^- skeleton absence because of limitation of the τ value. One more known rule indicates that the opening of the M^- ion cycle is accompanied usually by migration of H atom onto neighbouring C atom. This rule is also carried out for practically all FNIs of PBQ. There are only two exceptions: the FNIs with m/z 92 and 93, which are formed when the H atom walks onto more distant C atom. But in these two cases, the atoms H and C, which couple with each other in the dissociation product are possibly spatially close.

The formation of FNIs in PBQ has also some unusual for NIMS features. This is breaking of the double bonds and formation of a great number of FNIs with even m/z , which are unfavourable in energy ions-radicals with open shells. However, both phenomena can be explained by the structure features of PBQ, which allow compensating the corresponding energy expenditure. At disruption of the C=C bond in the M^- ion the compensation is provided by the additional double bonds formation in the fragments. For example, in FNIs with m/z 91, 93 and 94 five double bonds are formed, in FNIs with m/z 92—six, in contrast to four ones in the 'initial' M^- ion (Fig. 7). In this connection, it should be noted that the double-bond breakage takes also place at the formation of FNIs with m/z 41 which are well known from Ref. [6]. The expenditure of energy resulted from FNIs-radicals formation is compensated by producing of the corresponding neutral fragment in a molecule form, which leads always to a considerable gain in energy. For example, in case of FNIs with m/z 92, 82, 72, 66

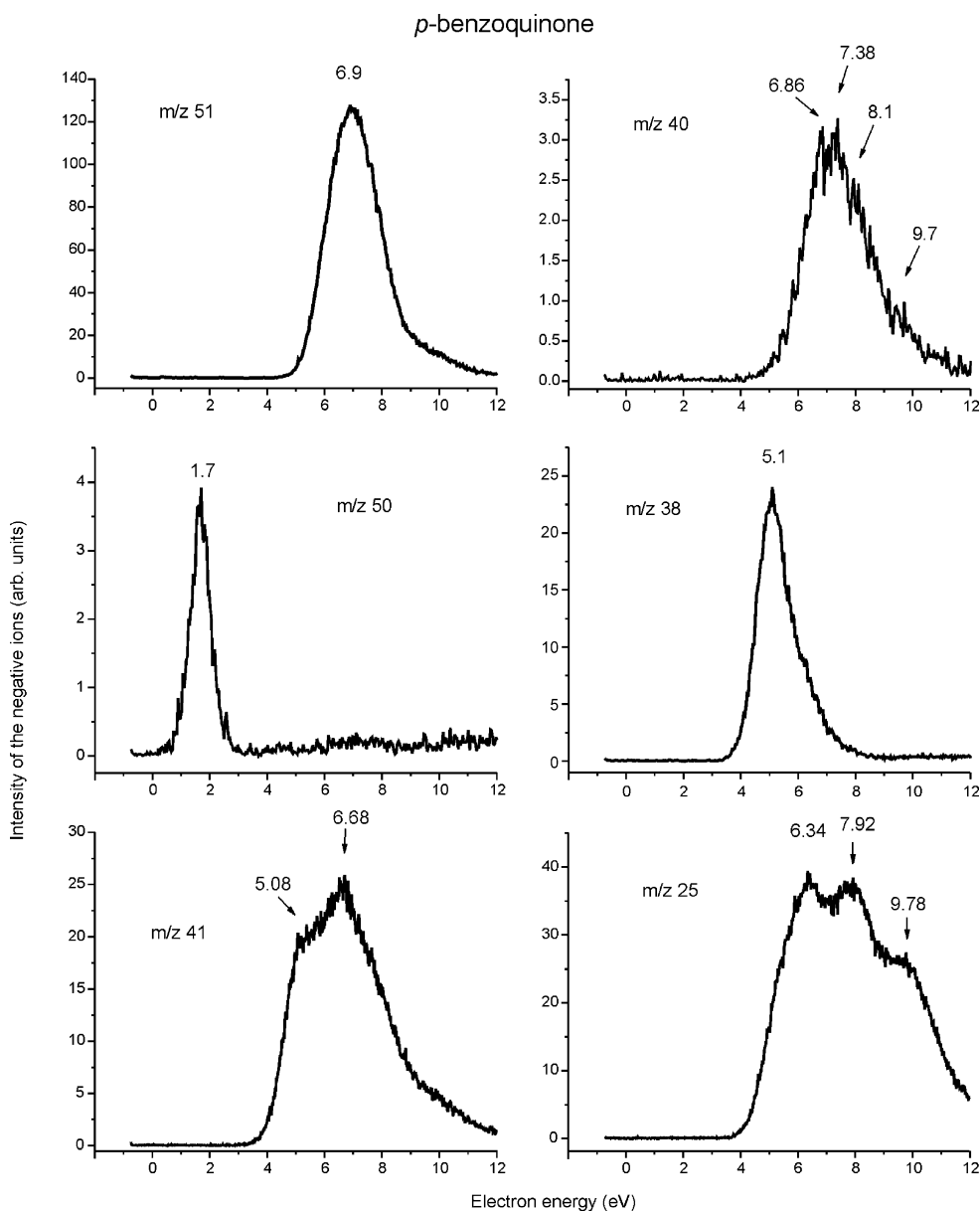


Fig. 6. Effective yield curves for negative ions with m/z 51, 50, 41, 40, 38 and 25.

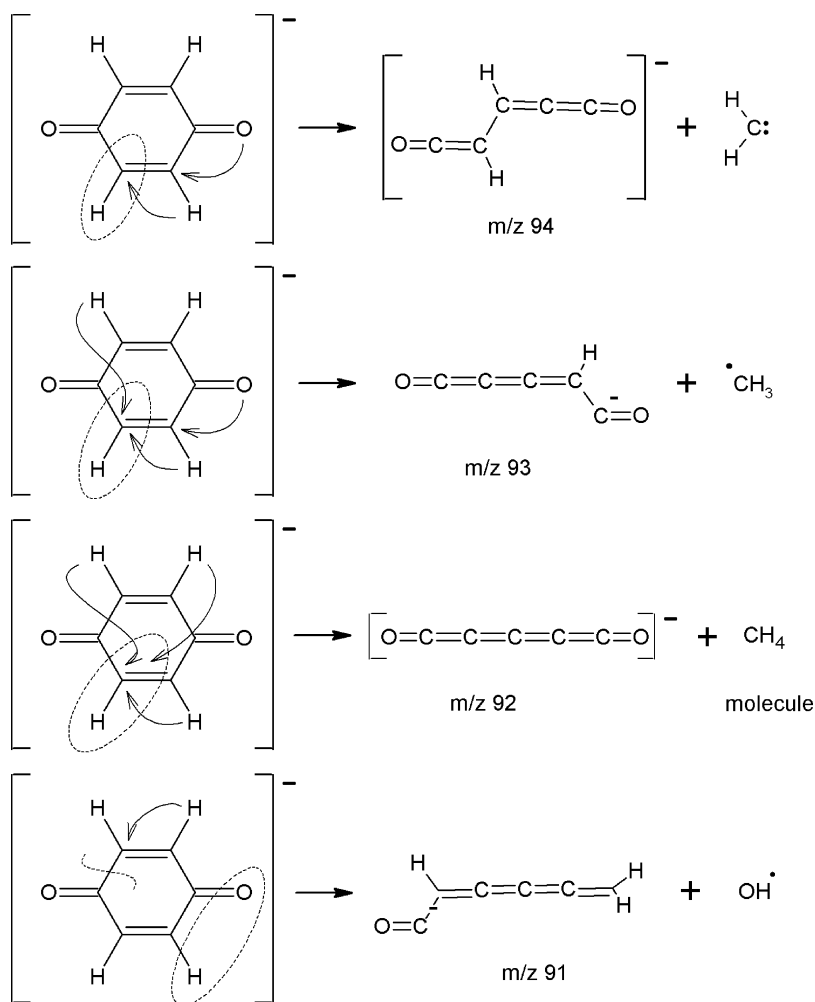
Fig. 7. Formation pathways of ions with m/z 94–91.

Table 1
Negative ion mass spectrum of resonance electron capture by molecules of *p*-benzoquinone

No	m/z	Ion structure	I (%)	E_{\max} (eV)
1	108	M^-	≈ 50	1.36*
			100	1.56
2	107	$[M-H]^-$	0.066	1.70
			0.067	4.86
			0.027	6.46
3	94	$[M-CH_2]^-$	0.14	1.26
4	93	$[M-CH_3]^-$	0.006	1.78
			≈ 0.003	5.78*
			0.004	6.78
5	92	$[M-CH_4]^-$	0.06	6.70
6	91	$[M-OH]^-$	0.012	5.58
7	82	$[M-C_2H_2]^-$	0.126	4.96
8	81	$[M-C_2H_3]^-$	0.012	2.38
			0.012	4.94
			0.029	6.9
			≈ 0.025	7.46*
9	80	$[M-CO]^-$	0.217	2.34
			0.045	5.02
10	79	$[M-COH]^-$	0.63	5.04
			≈ 0.27	6.36*
			≈ 0.225	7.17*
11	72	$[M-2H_2O]^-$	0.052	1.42
			0.003	6.42

Table 1 (Continued)

No	m/z	Ion structure	I (%)	E_{\max} (eV)
12	70	$[M-C_3H_2]^-$	0.065	1.42
			0.003	6.46
13	67	$[M-C_2, OH]^-$	0.022	5.18
14	66	$[M-H_2O, C_2]^-$	0.011	4.98
15	65	$[M-C_2H_2, OH]^-$	0.023	6.14
16	63	$[M-CO_2H]^-$	0.03	5.54
17	54	$[M-C_3OH_2]^-$	0.077	5.70
18	53	$[M-C_3OH_3]^-$	≈ 0.025	6.14*
			0.037	7.78
			≈ 0.01	9.74*
19	51	$[M-C_2O_2H]^-$	0.855	6.9
20	50	$[M-C_2O_2H_2]^-$	0.025	1.7
21	41	$[C_2OH]^-$	≈ 0.171	5.08*
			0.225	6.68
22	40	$[C_2O]^-$	0.02	6.86
			0.021	7.38
23	38	$[C_3H_2]^-$	0.162	5.10
24	25	$[C_2H]^-$	0.342	6.34
			0.333	7.92
			0.225	9.78*

(m/z) Mass-to-charge ratio; I , relative intensity; (E_{\max}) energy of maximum of effective yield curve; (*) 'shoulder' of effective yield curve; (bold type) ions known earlier (from Ref. [6]).

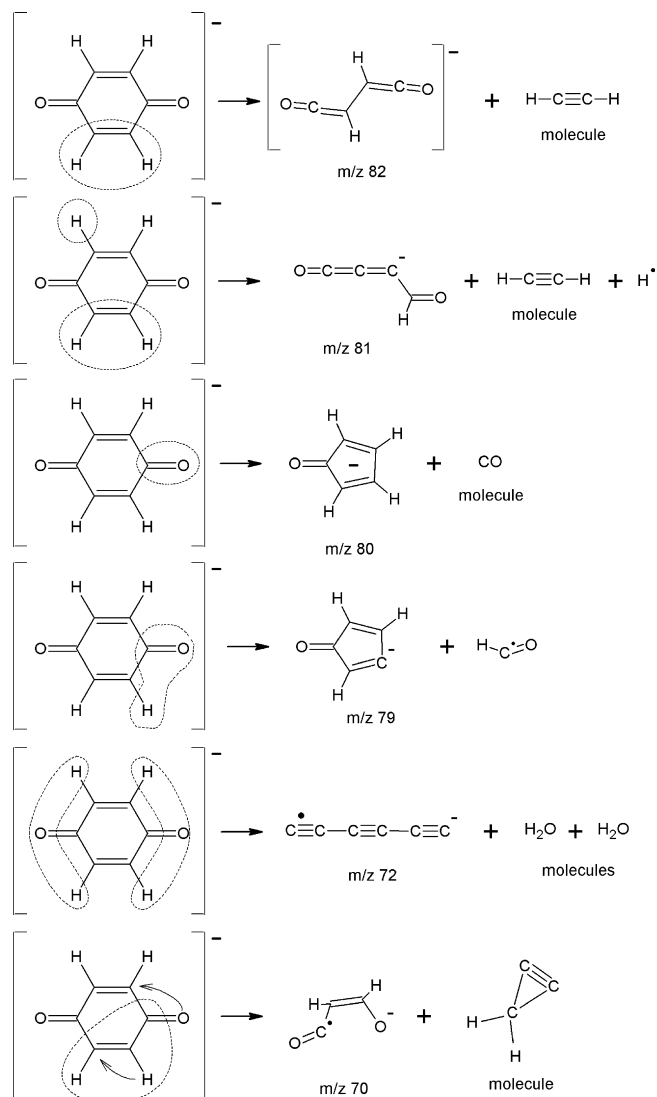


Fig. 8. Formation pathways of ions with m/z 82–79, 72 and 70.

and 40, there is an ejection of molecule of methane, acetylene, water, ethenone and furan, respectively (Figs. 7–10). The similar situation is also observed for the other FNIs-radicals. The sole exception is represented by FNIs with m/z 94 (Fig. 7), where the corresponding neutral fragment is methylene CH_2 . It is not a molecule. However, here the neutral fragment has also a closed shell like molecule.

The present work gives also new data on the resonant electron capture by PBQ molecules. As it was mentioned above, the EYC maximum of the M^- ions (Fig. 3, m/z 108) obtained here is placed at $E_{el} = 1.56$ eV that is above, than 1.35 eV known from Ref. [6] by 0.21 eV. This disagreement is probably caused by two factors: (i) the presence of two resonant states at 1.35 and 1.56 eV with different ion lifetimes, and (ii) an instrumental ion lifetime discrimination, which is different in both experiments. As a result, the intensity of the first state (at 1.35 eV) is maximal in the experiment of [6], whereas the intensity of the second one (at 1.56 eV) in the present work. The presence of two states of the long-lived M^- ions in PBQ can be confirmed, probably, by a shape of the I_{neu} neutrals EYC (curve b in Fig. 11), which was recorded along with the M^- ions EYC, using ETM (Fig. 11). Maximum at 1.56 eV and a 'shoulder' at 1.36 eV can be distinguished on curve b, which could mean two states described above. They can also be supported, perhaps, by a slight

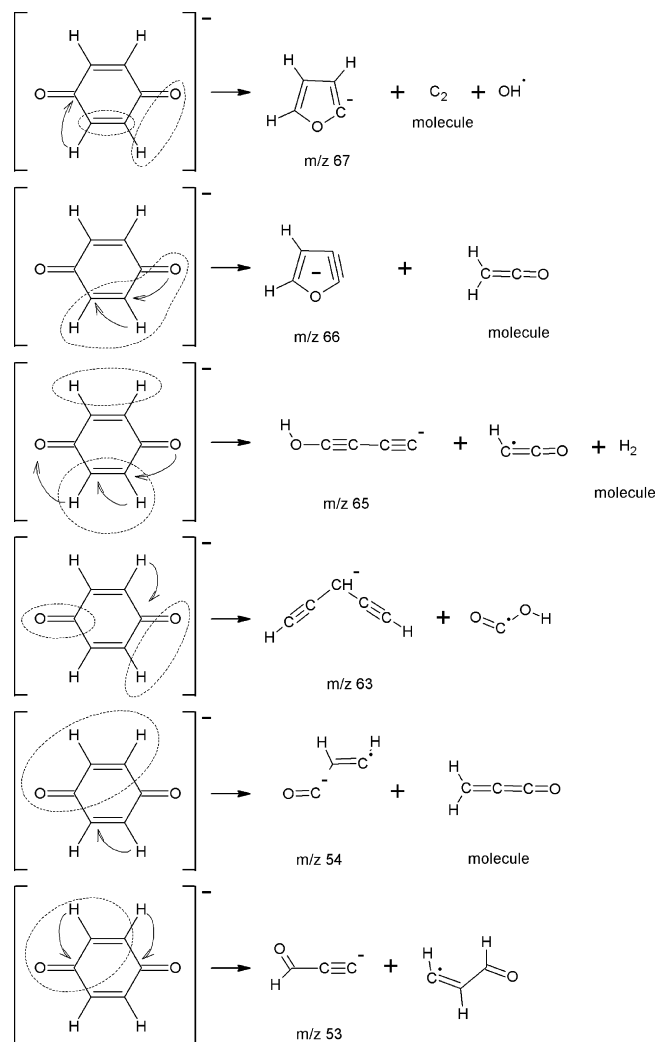


Fig. 9. Formation pathways of ions with m/z 67–65, 63, 54 and 53.

inflection point on the curve of the dependence: $\tau = f(E_{el})$ (curve d, Fig. 11), as well as by the M^- ions maximum energy spread obtained in different works. This maximum was registered at 1.35; 1.41; 1.43 and 1.6 eV in Refs. [6,16–18], respectively. The authors of work [6] also assumed presence of two states in the M^- resonant peak.

The information concerning the second state of the M^- ions of PBQ is important in determination of the resonant states number formed in PBQ at the low-energy region (1–2.5 eV), and finally for solving the abovementioned problem—identification of the electronic configurations of the M^- ions. According to the NI mass spectrum obtained in the present work, the M^- ions and FNIs with m/z 50, 71, 72, 80, 81, 93, 94, and 107 represent the region of 1–2.5 eV. Maxima of their EYCs are concentrated in three ranges: at 1.36; 1.56 and 2.35 eV. One can see that the first two of them are distinguished due to determination of two M^- states. With this result we can estimate a total number of the states, taking also into account two more resonances: at 0.7 and 1.9 eV invisible to negative ion mass spectrometry and registered earlier by means of 'SF₆ scavenger technique' in work [6]. Summarizing our data with the data of work [6], one can conclude that at least five resonant states: at 0.7, 1.36, 1.56, 1.9 and 2.35 eV, are formed, probably, in the low-energy region of the resonant electron capture by PBQ molecules.

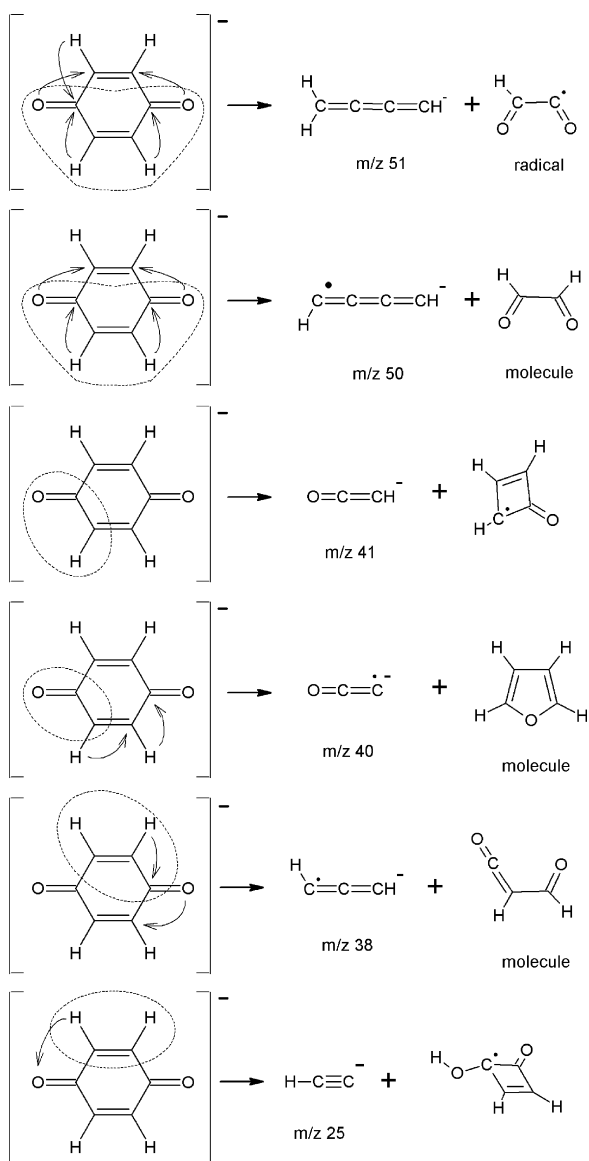


Fig. 10. Formation pathways of ions with m/z 51, 50, 41, 40, 38 and 25.

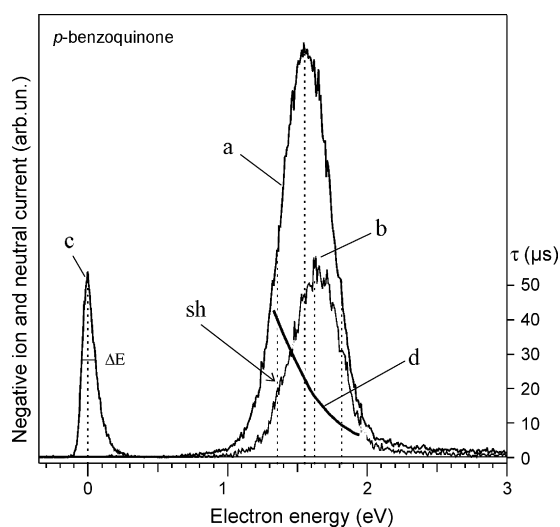


Fig. 11. Effective yield curves obtained with monochromator: long-lived M^- ions + neutrals (a); neutrals (b); SF_6^- (c); $\Delta E = 0.1$ eV; 'sh', 'shoulder'; lifetime (τ) of M^- ions as a function of E_{el} (d).

5. Conclusion

- The negative ion mass spectrum of the resonant electron capture by molecules of *p*-benzoquinone has been obtained, which is represented by ions of 24 types, among which only 6 types were known earlier.
- Schemes of the M^- ion fragmentation have been constructed for all dissociation channels. The schemes showed that structures of all fragmental ions correspond to *p*-benzoquinone gross formula, as well as to the known rules of the negative ions formation.
- For all ions constituting the negative ion mass spectrum of the resonant electron capture by PBQ molecule, the effective yield curves were recorded as functions of the attaching electron energy.
- The effective yield curves of PBQ long-lived M^- ions and the corresponding neutrals have been also obtained using monochromator with the electron energy distribution of 0.1 eV at the electron current of 0.1 μA . It was assumed that PBQ long-lived M^- ions are formed, possibly, in two resonant states close and poorly resolved in energy: at 1.36 and 1.56 eV. Then, in total, there are at least five resonant states in PBQ in the low-energy region: at 0.7, 1.36, 1.56, 1.9 and 2.35 eV.

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