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RESONANCE CAPTURE OF ELECTRONS AND PHOTOELECTRON SPECTROSCOPY

OF THE MOLECULES OF SUBSTITUTED ANISOLES AND THIOANISOLES

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In the electron resonance capture mass spectra of phenol, anisole, thioanisole, and their fluorinated analogs the resonances above 3.8 eV are electronically excited Fischbach resonances due to the excitation of the electron from several occupied MOs to one unoccupied MO. The mechanisms of the formation of the negative ions for these compounds are identical and do not depend on the nature of the heteroatoms. The low-energy resonances in the second energy region for PhR compounds (R = OH, OMe, SMe) correlate with the positions of the second singlet transitions. With thermal electron energies fluorinated anisoles are characterized by the formation of long-lived rearrangement ions. The absence of the rearrangement ion in fluorinated thioanisole can be explained by the energetically less favorable removal of the neutral CHF=S fragment compared with the CHF=O fragment for fluorinated anisole.

Earlier it was shown that thiophenol [1] and thioanisole [2] form negative ions (NI) in several regions of electron energies under the conditions of electron resonance capture (ERC). In the present work we studied benzene derivatives C_6H_5R, where R = OH (I), OCH_3 (II), SCH_3 (III); and C_6F_5R', where R' = $OCHF_2$ (IV), $SCHF_2$ (V), $OCHCl_2$ (VI) by negative-ion ERC mass spectrometry and tried to interpret the mechanisms of the formation of the negative molecular ions (NMI) by means of the data from UV and photolectron (PE) spectroscopy and also MNDO quantum-chemical calculations.

EXPERIMENTAL

The negative-ion ERC mass spectra were obtained on an MX-1303 mass spectrometer which had been adapted for recording negative ions. The electron energy scale was calibrated and the electron distribution with respect to the energies was monitored from the type of curve for the effective yields of SF_6^- ions from SF_6. For calibration of the high-energy resonances we used benzene, which forms $(M-H)^-$ ions with a maximum at 8 eV. The electron distribution with respect to energies amounted to 0.3-0.4 eV at the half-height, and the electron current corresponded to 1 μA. The error in the determination of the maximum was ±0.1 eV. The PE spectra were obtained by excitation of the molecules with He-I radiation having quan-
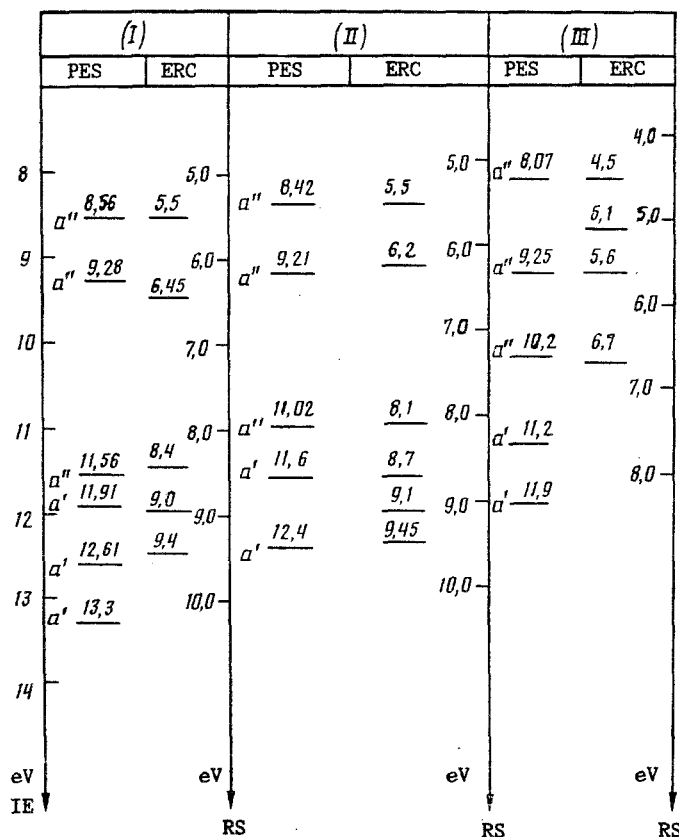

Fig. 1. Correlation diagram of the ionization energies and
resonance states.

tum energy of 21.21 eV. The kinetic energy scale of the photoelectrons was calibrated a-
gainst the lines of xenon (IE_1 = 13.13 and IE_2 = 13.43 eV). The error in the determination
of the maxima of the ionization bands was not greater than 0.03 eV. The quantum-chemical
calculations were conducted by the MNDO method with optimization of the geometry in the sp
basis set.

RESULTS AND DISCUSSION

The positions of the vertical ionization energies (IE) of compounds (I-VI), obtained
from the photoelectron spectra [IE of compounds (I, II, III) from data in [3, 4, 5]], are
given in Figs. 1 and 2. In (I-III) in the region of 7-11.6 eV there are three bands. Mix-
ing of the highest occupied MOs with a coplanar arrangement of the unshared electron pairs
(UEP) of the sulfur and oxygen atoms and the π-MO leads to the formation of antibonding (n −
b_1) and bonding (n + b_1) combinations of the MOs. The calculations show that the introduc-
tion of the F atom into the benzene ring does not lead to a substantial change in the nature
of the interaction between the b_1 orbital and the UEPs of the S and O atoms. However, the
presence of the F atoms has an effect on the energy of the MO. It was shown by x-ray fluo-
rescence spectroscopy that in the PhF molecule the 2p-AO of the F atom hardly interacts at
all with the highest occupied π-MOs of the ring on account of the large difference in energy
[6]. There are no grounds to suppose that the introduction of several F atoms would radi-
cally change the situation in benzene derivatives. In the absence of orbital overlap the F
atom will change the energy of the π orbital predominantly by electrostatic interaction of
the electrons which occupy these MOs with an effective positive charge developing at the C
atom attached to the F atom. Thus, for fluorinated anisole and thioanisole the first ioniza-
tion bands are equal to 10.06 and 10.13 eV, the values of which are 1.64 and 2.33 eV higher
than the first IEs in anisole and thioanisole. Increase in the number of F atoms to six in
the benzene ring leads to degeneracy in the first two MOs (hexafluorobenzene). From the PE
spectra for pentafluorophenol and pentafluoroanisole it is seen that substitution of the F
atom by the donating groups OH and OCH_3 does not lead to removal of the degeneracy [7]. On
the other hand, it was observed in [8] that in α-halogenoanisoles the angles between the
plane of the benzene ring and the methoxy group are 56° for $PhOCH_2F$, 45° for $PhOCH_2Cl$, and
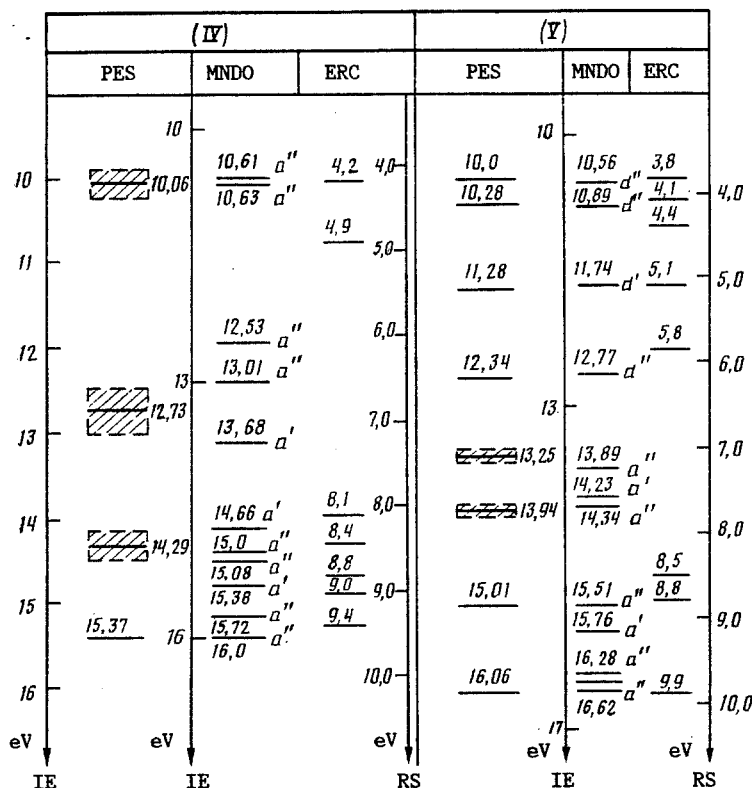
Fig. 2. Correlation diagram of the ionization energies, resonance states, and ionization energies obtained from the MNDO quantum-chemical calculations. (The dotted line shows the half-width of the ionization bands.)

90° for $PhOCHF_2$ and $PhOCF_3$, indicating that the CHF_2 and CF_3 groups are perpendicular to the plane of the benzene ring. This is confirmed by the PE spectra for $C_6F_5OCF_3$ [9]. As shown by the calculations, the rotation of the $SCHF_2$, $OCHF_2$, and $OCHCl_2$ groups leads to degeneracy in the first two MOs of the benzene ring. In fact, the first three lines in the PE spectra of (I-III) are clearly separated, whereas appreciable broadening of the bands is observed in (VI, V). Determination of the areas of the first ionization bands indicates that the first of them contains at least two MOs. As in the cases of pentafluorophenol and pentafluoroanisole, the first two bands in compounds (IV-VI) are evidently degenerate. Quantum-chemical calculations confirm this suggestion (Fig. 2). Thus, the contribution to the first MO from the UEP of the O atom for compound (IV) amounts to ~3%, while the contribution from the UEP of the S atom for (V) amounts to ~1%.

The main processes in the dissociation of the negative molecular ions (I-III) take place with cleavage of the C—S, C—O, and H—O bonds. The mass spectra also contain fragment ions due to cleavage of the benzene ring (Table 1). It is possible to single out three regions of electron capture. The S^- and PhS^- ions are observed in the first, the CH_3^-, SCH_3^-, $C_6H_5^-$, and $C_6H_3^-$ ions in the second, and ions due both to dissociation of the benzene ring and to direct cleavage of the bonds are observed in the third. The fluorination of the molecules increases the lifetime of the negative molecular ion, and this promotes the occurrence of rearrangement processes slower than simple bond cleavage. For example, during the capture of thermal electrons by the molecules of (IV, VI) the rearrangement ions $C_6F_6^-$ for (IV) and $C_6F_5Cl^-$ for (VI) are formed (Table 1). The average lifetimes of these ions with respect to the autoelimination of electrons are 180 and 215 μsec, respectively, which is significantly higher than in the $C_6F_6^-$ ions from C_6F_6 (12 μsec). This indicates that the reserve of internal excitation energy in the rearrangement ion $C_6F_6^-$ is appreciably less than in the molecular ion from hexafluorobenzene and confirms that the given ions are formed as a result of a rearrangement process, which takes place with cleavage of the C—O bond and migration of the halogen atom to the ipso position of the ring. The quantum-chemical calculations showed that the CHF_2 group in (IV) and (V) is withdrawn from the plane of the ring. Since the symmetry of the initial and final states coincides, the absence of the rearrangement ion $C_6F_6^-$

TABLE 1. Relative Intensities of the Total Currents (% of I_{max}) at the Maxima of the Resonances (eV) in the Negative-Ion Mass Spectra of Anisoles and Thioanisoles

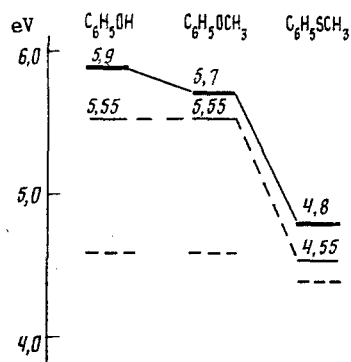| C6H5OH (I)		C6H5OCH3 (II)		C6H5SCH3 (III)		C6F5OCHF2 (IV)		C6F5SCHF2 (V)		C6F5OCHCl2 (VI)	
m/z	I, %	m/z	I, %	m/z	I, %	m/z	I, %	m/z	I, %	m/z	I, %
93	100(1,2) 0,5(5,5) 0,3(6,8) 2(8,4)	107	30(8,1)	123	0,7(8,4)	234 215	20(0,0) 0,4(4,9) 0,3(8,1)	231	0,07(5,1)	228	0,8(4,9)
92	1,3(9,0)	105	3(8,1)	109	100(0,75) 0,3(5,1) 0,6(10,0)	195	0,015(4,2) 0,07(8,4)				
77	0,2(8,45)	93	44(1,2) 16(5,5) 10(6,15) 24(9,1)	108	1,1(8,9)	186	100(0,1)	199	100(0,0) 18(4,1)	202	100(0,0) 0,8(4,2)
						183	0,4(4,2) 2,6(8,8)			183	0,2(4,3) 0,3(6,5)
		92	100(8,7)	77	1(5,6) 1,8(6,7) 2,4(8,45) 1,9(10,5)	167	2,6(4,2) 2,6(8,8)	167	5,5(4,1) 0,6(9,9)	167	0,4(4,3) 0,3(6,5)
						164	0,2(4,9) 0,6(8,8)	180	0,1(3,8) 0,7(8,8)		
25	0,25(10)	77	28(8,25)	75	0,9(5,6) 1,9(6,7) 2,4(8,45)	148	0,08(4,3) 0,03(10,5)	148	0,1(4,1)	148	0,01(4,5)
						129	0,5(9,4)				
		75	8,8(9,05)	65	0,05(8,4)	39	4(4,2)	39	0,2(4,4)	71	0,9(4,4)
		65	7(6,3) 7(8,15)	47	0,8(4,55) 1,4(8,45)	19	0,3(4,8) 1,8(10,8)	19	0,3(5,8) 0,3(8,5) 0,2(10,5)	19	0,05(5,8) 0,1(8,5) 0,1(10,5)
		31	7(5,5) 3(6,1) 60(9,45)	33	0,12(9,1)			51	1,6(4,1)		
		25	20(9,4)	32 15	0,14(1,2) 0,07(8,6) 2,6(4,55)					35	27(0,5) 2(4,6) 1,3(7,0)

Fig. 3. Correlation diagram between the energies of the
second singlet transitions and energies of the low-energy
resonance states in the second energy region. The bold
lines show the energies of the second singlet transitions,
the faint lines show the energies of the resonance states,
and the dotted lines show the energies of the first singlet
transitions. The energies of the respective states are
given in parentheses.

in (V) can evidently be explained by the energetically less favorable removal of the neutral CHF=S fragment compared with the CHF=O fragment. In the mass spectrum of $C_6F_5OCH_3$ the rearrangement ion $C_6F_5H^-$ is absent, and this is probably due both to the lower electron affinity of C_6F_5H compared with C_6F_6 and C_6F_5Cl [10] and to the larger energy for cleavage of the C—H bond compared with the C—F and C—Cl bonds [11].

Figure 1 shows the energy positions of the maxima of the resonance states (RS) in the molecule—electron system, determined from the curves for the total ion current in the mass spectra of (I-V). The scales for the IE and RS are given in one scale for each compound and are combined in such a way that the position of the first resonance in the second energy region coincides with the first IE with respect to energy. With such an arrangement of the two scales it is clearly seen that the energy gaps between the majority of the resonance states and the ionization energies coincide with an accuracy of 0.1-0.3 eV. From this it follows that the resonances are electronically excited Fischbach resonances due to excitation of the electron from several occupied MOs (OMO) to one and the same unoccupied MO (UMO) [12]. It must be emphasized that the mechanism of the formation of the negative ion in anisole, phenol, and thioanisole is the same and does not depend on the nature of the heteroatom O or S. The question of the UMO at which excitation of the electrons occurs in the series of OMOs then arises. We make use of the fact that the first resonances in the second energy region correlate with the energies of the second singlet excited states of the molecules (Fig. 3), and the energies of electron affinity for (I-III) are approximately identical and amount to 0.3-0.4 eV.* On the other hand, the monomolecular dissociation of the negative molecular ion must take place without change in the symmetry of the electronic state [14]. For the fulfillment of this requirement it is necessary to assume that the three electrons are in different MOs: one electron is in the UMO which correlates with the second singlet transition, the second is in a fully symmetric Rydberg orbital, and the third is in the OMO [15]. In view of the fact that the investigated molecules belong to the C_s symmetry group, all the orbitals will be either symmetric (a') or antisymmetric (a") in relation to the plane of the benzene ring. The symmetry of the occupied MOs according to the quantum-chemical calculations is shown in Figs. 1 and 2. The spectroscopic state of the negative molecular ion for the first electronically excited Fischbach resonance is then A" × A" × A' = A'. The electronic ground states of the (M—H)⁻ and (M—CH₃)⁻ ions belong to A' representations, according to the results from the calculations, and the states of the H atom and the CH₃· radical also belong to A'. Comparing the direct product of the state of the dissociation products, we

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*The UV absorption spectra for compounds (I-III) have two bands in the region of 200-300 nm. The long-wave band with a maximum at 260-280 nm can be assigned to the $A_{1g} \rightarrow B_{2u}$ transition of the π electrons of the benzene ring. The short-wave band in the region of 210-240 nm belongs to the $A_{1g} \rightarrow B_{1u}$ transitions in the benzene ring [13].

obtain: A' × A' = A'. The possibility of the investigated dissociation process is demonstrated by similarity in the result from the direct product with the spectroscopic state of the negative molecular ion. A similar pattern is observed for the formation of the OCH_3^- and CH_3^- ions. The ions in the electronic ground state belong to the A' representations, and the $C_6H_5\cdot$ radical also belongs to A'. The formation of the CH_3^- ion is an interesting case; this ion is evidently formed not by direct cleavage of the C—S bond in the negative molecular ion but by successive dissociation. For the process

$$C_6H_5SCH_3^- \; (A') \rightarrow C_6H_5S^\cdot \; (A'') + CH_3^- \; (A')$$
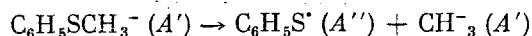
the direct product of the dissociation products A" × A' = A" does not contain the A' representation, and this demonstrates that this process is impossible. The observed dissociation with the formation of the CH_3^- ion evidently takes place according to the following scheme:

$$C_6H_5SCH_3^-(A') \rightarrow C_6H_5^\cdot(A') + SCH_3^-(A') \rightarrow C_6H_5^\cdot(A') + $$
$$+ S(A') + CH_3^-(A')$$
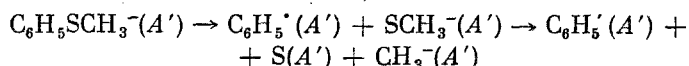
In this case the direct product contains A', which signifies that this process is possible, and it is confirmed by the effective yield curve of the SCH_3^- and CH_3^- ions. In the second energy region the resonance energy of the parent ion SCH_3^- is displaced by ~0.15 eV toward lower electron energies in comparison with the resonance energy of the daughter ion CH_3^-. A consistent pattern is also observed for the formation of the $C_6H_5^-$ ion for (III). The orbital of the $SCH_3^\cdot$ radical belongs to the irreducible representation of the E group of C_{3v} symmetry and is split into two states A' + A" in the C_s group, while the electronic ground state of the $C_6H_5^-$ ion is A'. Hence, A' × (A' + A") = A' + A". The spectroscopic states of the negative molecular ion in the first, second, and third resonances are A', A", and A', respectively. Since the direct product contains the A' and A" representations, the described dissociation is possible. During examination of the mechanisms of the formation of the resonances (Fig. 1) it is seen that the resonance at 5.1 eV for thioanisole does not fit into the indicated scheme. In fact, this resonance state must correspond to an IE with energy of 8.6 eV. In [4] the temperature dependence of the PE spectrum of PhSMe was studied in the range of 20-500°C, and it was shown that the conformer with the nonplanar arrangement of the substituent can exist in the gas phase. The first IE mainly has the character of the "pure" UEP of the S atom and is equal to 8.55 eV. In order to determine the nature of the resonance at 5.1 eV we also studied the temperature dependence of the mass spectrum of (III) in the range of 20-400°C. With increase in temperature a change in the form of the curve for the negative ion CH_3^- and in the yield of the individual fragment ions was observed together with a general increase in intensity. With increase in temperature the effective yield curve of CH_3^- becomes more symmetrical, and this evidently indicates a relative increase in the formation of the second conformer, as a result of which the maximum of the effective yield curve is shifted toward larger energies. Increase in temperature also leads to an increase in the relative yield of the negative ion, due to cleavage of the C—S bonds. The mechanism of electron capture is less clearly defined for (IV) and (V), in which the ionization bands are broad and poorly resolved (Fig. 2). However, the satisfactory correlation of the quantum-chemical calculations both with the PE spectra and with the ERC spectra makes it possible to state that the electron capture mechanisms for (IV), (V), and (I-III) are similar.* In turn this makes it possible to isolate the IEs from the broad unresolved ionization bands. Thus, for example, the PE spectrum of fluorinated anisole can be represented by the following IEs: 10.06, 10.16, 11.9, 12.4, 13.0, 14.0, 14.4, 14.5, 13.8, 15.1, 15.4.

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*The resonances at 4.9 eV for (IV) and 4.4 eV for (V) do not fit into the scheme presented above and are probably electronically excited resonances due to the other unoccupied MO.

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CRYSTAL STRUCTURE OF 1,1,1,2,2-PENTAFLUORO-3-AMINOHEX-3-EN-5-ONE AND

ISOMERIZATION OF β-AMINOVINYLKETONES AND β-AMINOVINYLTHIONES CONTAINING

FLUORINE

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The x-ray structure of 1,1,1,2,2-pentafluoro-3-aminohex-3-en-5-one has been solved. Isomerization of β-aminovinylketones and β-aminovinylthiones containing fluorine occurs with significant rearrangement of the molecular packing in the crystal apparently through a bimolecular mechanism.

Fluorine-containing β-aminovinylketones (AVK) (I) and their thioanalogs β-aminovinylthiones (AVT) (II) with an amino group in the gem-position relative to the fluoroalkyl substituent isomerize into AVK (III) and AVT (IV), respectively, apparently through an intermolecular mechanism [1, 2]

$R^F = CF_3$, C_2F_5, C_3F_7, $H(CF_2)_2$; $R^1 = Me$, Ph; $R^2 = H$, Me; $X = O$ (I), (III), S (II), (IV).
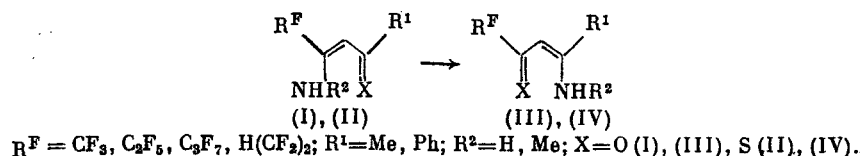
Isomerization occurs not only on heating but also on prolonged storage at 20-25°C of crystals of the low-melting compounds.* This is consistent with a localized mechanism for this reaction.

In order to verify this hypothesis, we solved the x-ray structure of 1,1,1,2,2-pentafluoro-3-aminohex-3-en-5-one (Ia). A general view of (Ia) is shown in Fig. 1. Bond angles are given in Table 1.

The (Ia) molecule, with the exception of the perfluoroethyl group, is planar within 0.007(2) Å. Atom C^2 deviates from this plane by 0.124(2) Å. The geometry is stabilized by

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*The crystals gradually soften, darken, and change into a brown oil which is a mixture of isomers (I) and (III) [or (II) and (IV)] according to TLC or preparative separation.