monoisotopic form and their elemental compositions were calculated by the use of the "AELITA" program [10]. Metastable transitions were measured by the defocusing method.

Compounds (II)-(IV) and (VII) were obtained in accordance with [2]; compound (V) was obtained from (II) by hydrolysis with water adsorbed on silica gel. Compounds (I) and (VI) were also obtained from (II) by the action of LiAlH₄ and HC(OC₂H₅)₃, respectively.

**SUMMARY**

1. A study has been made of the mass spectra of tricarbonyliron complexes of 1-sila-2,4-cyclohexadiene with various substituents on the silicon atom.

2. The main route of fragmentation of the tricarbonyliron complexes under electron impact is successive decarbonylation with subsequent elimination of an HR molecule with the participation of the iron atom.

3. Structures have been proposed for the ions C₅H₅SiRFe⁺, C₅H₅Si⁺, and C₃H₃Si⁺. In the decomposing C₅H₅SiRFe⁺ ions, interaction of the iron atom with the silicon atom takes place, whereas the nondecomposing ions probably have the structure of coordinated silabenzene. A pyramidal structure of the nido-cluster type is ascribed to the C₅H₅Si⁺ and C₃H₃Si⁺ ions.

**LITERATURE CITED**


**MASS SPECTRA OF NEGATIVE IONS OF ANABASINE AND ESTERS OF LUPININE**

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A few scientists have been studying the processes of low-energy (0-15 eV) electron capture by polyatomic molecules by mass spectrometry for more than ten years. However, a systematic study of the effect of the functional groups on negative ion formation by polyatomic molecules is essentially only just beginning, and the first results relate to chemically and biochemically important compounds whose molecules contain the benzene ring [1-3]. Being a continuation of this work, the present article is devoted to a study of electron capture by the molecules of anabasine (I) and esters of lupinine (II)


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It seemed to us to be interesting to investigate the effect of substituents on the lifetime ($T$) of negative molecular ions (NMI) with respect to the autocleavage of an electron and on the dissociative electron capture (DEC) by molecules. The compounds investigated have a wide spectrum of physiological activity and are interesting pharmacologically; the mass spectra of the positive ions of these compounds have been studied previously [4, 5].

The mass spectra were recorded on a modernized MKh-1303 mass spectrometer, adapted to register negative ions; $T$ was measured by the method described in [6].

The NMI were registered mass spectrometrically ($T(M^-) \approx 10^{-6}$ sec) for $R = NO_2$, Br, and Cl. The results of $T(M^-)$ measurements, $\mu$sec, were: 1050 ($NO_2$), 66 (Br), 42 (Cl) for (I) and 1200 ($NO_2$), 64 (Br) for (II). Hence it can be seen that within the limits of error for the $T(M^-)$ measurement, compounds (I) and (II) are identical for the same substituents, and in the case of a substituent with acceptor properties, $T(M^-)$ increases by more than one order. In other words, the lifetime of NMI with respect to electron autocleavage from such comparatively large molecules is sensitive to the donor-acceptor properties of the substituent, and sharply increases when the latter decreases the charge density of $\pi$ electrons of the benzene ring [1]; a variation of substituent-donors has little effect on $T(M^-)$.

The above-indicated NMI were formed by thermal electrons with almost zero energy by means of the vibratory-excited Feshbach resonance, i.e., molecules with $R = NO_2$, Br, and Cl have a positive electron affinity. However, if the maxima of effective yield curves (EYC) for $M^-$, when $R = Br$ and Cl coincide with the EYC maxima for ions of the reference gas $SF_6^-$, and the form of these curves coincides completely with the $SF_6^-$ curve, then when $R = NO_2$, the EYC for the resonance peak half-height are 0.1-0.15 eV broader, possibly because of deformation changes in the molecule following electron capture. Moreover, for (II) when $R = NO_2$ we recorded a second resonance peak for $M^-$ at $\approx 2.2$ eV with $\tau(M^-) = 250 \mu$sec. The relatively greater energy observed for NMI in this case provides support for the electron-excited Feshbach resonance, but the possibility indicated in [1] should also be taken into account, i.e., that when two acceptor substituents are added to the benzene ring in the $p$ position, not only the first vacant orbital, but also the second, can be below the occupied orbital of the neutral molecule, and in this case the NMI will be formed in the two states, though by the same mechanism.

Apart from the positive value of the electron affinity, $\tau(M^-)$ depends on many parameters, including $N$, the number of vibrational degrees of freedom [7]. However, in order to compare the $\tau(M^-)$ values of compounds (I) and (II) from this viewpoint, it is necessary to know the electron affinity values. The experimentally observed similarity of $\tau(M^-)$ values for compounds with an identical $R$ can apparently be interpreted by the presence in these compounds of the common electrophilic center $-CO-\bigcirc--R$, responsible for the nondissociative electron capture. This means that during electron capture the excess energy is distributed in the vibrational degrees of freedom not of the whole molecule but only of the aforementioned center at which the electrons are delocalized; for both types of molecules conjugation is disturbed beyond the carbonyl group, but for compounds (II) the remaining molecular block is in general fully saturated. The lifetime $\tau(M^-)$ is more critical to the length of the conjugation chain than to the size of the whole molecule, as can be seen by comparing $\tau(M^-)$ for nitrobenzene and nitrophenyldioxane [8] with (I) and (II) ($R = NO_2$), measured by the same method under identical conditions: 48, 83, 1050, and 1200 $\mu$sec, respectively.

Substituents such as NH$_2$, CH$_3$, and OCH$_3$, when in the $p$ position to the NO$_2$ group in nitrobenzene, give rise to long-lived NMI [1]. These same donor groups, when in the $p$ position to the weak acceptor group CO at the $-CO-\bigcirc--R$ active center of molecules (I) and (II) do not give rise to long-lived NMI; the electron affinity of such molecules is apparently negative.

(I): R = NO$_2$, Br, Cl, OCH$_3$, and CH$_3$. (II): R = NO$_2$, Br, NH$_2$, and CH$_3$. It seemed to us to be interesting to investigate the effect of substituents on the lifetime ($\tau$) of negative molecular ions (NMI) with respect to the autocleavage of an electron and on the dissociative electron capture (DEC) by molecules. The compounds investigated have a wide spectrum of physiological activity and are interesting pharmacologically; the mass spectra of the positive ions of these compounds have been studied previously [4, 5].