Russian Chemical Bulletin, International Edition, Vol. 54, No. 5, pp. 1121—1124, May, 2005

Electron affinity and suppression effect in analysis of chlorofullerenes by MALDI mass spectrometry

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Samples of the recently obtained higher chlorides of fullerenes C_{60} and C_{70} were analyzed by MALDI mass spectrometry. These systems exhibit the suppression effect of signals from the main components compared to signals of admixtures. A model was proposed to explain this effect by the Bell—Evans—Polanyi principle taking into account specific features of the structures and electron-withdrawing properties of different fullerene chlorides. The model is of general character and can be used for description of different suppression effects using MALDI mass spectrometry.

Key words: fullerenes, chlorination, chlorofullerenes, MALDI mass spectrometry, suppression effect, electron affinity.

The use of the previously proposed method for fullerene chlorination enabled us to discover several high fullerene chlorides: $C_{60}Cl_{24}$,[1] $C_{60}Cl_{28}$,[2] $C_{60}Cl_{30}$,[3] and $C_{70}Cl_{28}$.[4] These compounds were studied by diffraction and spectroscopic methods and MALDI (matrix-assisted laser desorption/ionization) mass spectrometry. Analysis of the $C_{60}Cl_{24}$ and $C_{70}Cl_{28}$ samples with the admixture content <5% gave contradictory results. As should be expected, the $C_{70}Cl_{27}^-$ anions, which formed by dissociative electron trapping by the $C_{70}Cl_{28}$ molecules with chlorine atom loss, predominated in the mass spectrum of the $C_{70}Cl_{28}$ sample. At the same time, an unexpected result was obtained for the $C_{60}Cl_{24}$ sample: the signal corresponding to the $C_{60}Cl_{27}^-$ anion was the most intense, although the sample contained $C_{60}Cl_{28}$ only as an insignificant admixture. Until presently, the MALDI mass spectra of chlorofullerenes always exhibited inverse ratios, namely, a considerable underestimation of intensities of ions corresponding to compounds with a higher chlorine content, due to their noticeable thermal dissociation.[5—7] It is difficult to perform quantitative analysis by the MALDI method because of a diversity of chemical transformations in a laser-induced jet, resulting finally in a discrepancy in molecular compositions of the analyzed mixture and detected ions. This phenomenon was studied most completely for the formation of protonated molecular ions, designated in literature as "Analyte Suppression Effect" (we will use the term "suppression effect"), and described in detail in the review.[8] Thus, the suppression effect is observed for chlorofullerenes analyzed by the MALDI method. In this case, this effect has a new, earlier undescribed nature. In the present work, we attempted to theoretically explain the new manifestation of the suppression effect.

Experimental

Individual compounds $C_{60}Cl_{24}$ and $C_{70}Cl_{28}$ with an admixture content <5% were synthesized by the reactions of fullerenes C_{60} (or $C_{60}Br_{24}$) and C_{70} with inorganic chlorides $SbCl_5$ and VCl_4 according to a previously described procedure.[1] A comparison of the experimental and calculated IR spectra of the $C_{60}Cl_{24}$ sample indicated unambiguously the presence of isomer $C_{60}Cl_{24}$ of symmetry T_h, which was further confirmed by the X-ray single crystal diffraction study.[9] The structure of $C_{70}Cl_{28}$ was also determined by X-ray diffraction.[4]

Experiments on laser desorption/ionization were carried out on a Voyager-DE MALDI-TOF mass spectrometer equipped with a UV laser (λ = 337 nm, pulse duration 3 ns, frequency 20 Hz). A laser beam was directed to a target at an angle of 45°; the laser beam energy exceeded insignificantly the threshold of ion current detection. All measurements were conducted in a linear mode with delayed ion flight-off at an accelerating voltage of 20 kV. Spectra were obtained in the negative ion detection mode with accumulation of single laser pulses.

Commercial preparation DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile), which was

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Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 1093—1096, May, 2005.

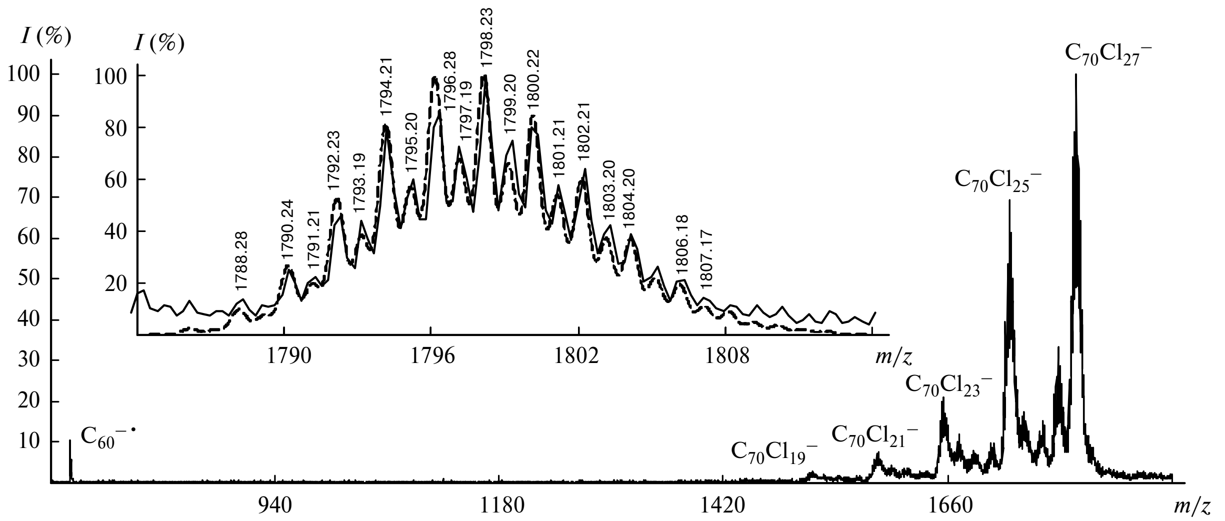

Fig. 1. Mass spectrum of negative ions in $C_{70}Cl_{28}$. The peak with *m/z* 720 corresponds to the radical anion of fullerene C_{60} added to the sample for internal calibrating. The insert shows the correspondence between the experimental (solid curve) and theoretical (dotted curve) isotope distribution for the $[C_{70}Cl_{27}]^-$ anion (resolution 2200).

dissolved in acetone (concentration 10 mg mL^{-1}), was used as a matrix. Chlorofullerenes were dissolved in toluene in an average concentration of 1 mg mL^{-1}. Samples for analysis were prepared by mixing the corresponding volumes of the starting solutions in such a way that the molar ratio between the matrix and sample would be 1000 : 1. For internal two-point weight calibration, several microliters of a toluene solution of C_{70} were added to the chlorination products of C_{60} and, *vice versa*, a solution of C_{60} was added to the chlorination products of C_{70}. A sample of the mixture (1 μL) was supported on a stainless steel plate. The solvent was removed by a dry air flow before the sample was loaded into the ion source of a mass spectrometer.

Results and Discussion

The mass spectrum of negative ions from compound $C_{70}Cl_{28}$ is presented in Fig. 1. The most intense lines correspond to the $C_{70}Cl_{27}^-$ and $C_{70}Cl_{25}^-$ anions with the closed electronic shell. The assignment of peaks corresponds completely to the isotope distribution in the chlorofullerenes (see insert in Fig. 1). We also discovered an admixture of oxochlorides containing from one to three oxygen atoms in the molecules. The presence of the signals from $C_{70}Cl_{25}^-$ can be explained by the formation of $C_{70}Cl_{26}$ molecules due to thermal dissociation of the sample upon laser evaporation or to the presence of a small amount of this compound in the starting sample. The resulting spectrum, which contains no signals with *m/z* exceeding those for $C_{70}Cl_{27}^-$, indicates unambiguously that $C_{70}Cl_{28}$ is the final product of the synthesis, *i.e.*, compounds containing more than 28 Cl atoms are not formed.

The MALDI method was used to analyze samples with a more complex composition. The mass spectrum of negative ions from a mixture of chlorides, which was prepared by the chlorination of [60]fullerene with antimony pentachloride at room temperature and containing on the average, according to the chemical analysis data, less than 24 C atoms per C_{60} molecule, is shown in Fig. 2. The most intense peaks (in the order of decreasing their intensity) correspond to ions containing 21, 23, 19, 25, 17, and 27 Cl atoms. This result does not contradict the chemical analysis data and can be used for identification of components in a complex mixture of chlorofullerenes.

The mass spectrum of negative ions in compound $C_{60}Cl_{24}$ containing several percentage $C_{60}Cl_{28}$ as an admixture is shown in Fig. 3. A good isotope resolution allows the unambiguous assignment of the detected ions to fullerene chlorides. Evidently, the procedure used in this work made it possible to avoid thermal dissociation of this compound, because the spectrum exhibits virtually no ions containing less than 23 Cl atoms. However, the most interesting and unexpected result is that the intensity of signals from the $C_{60}Cl_{23}^-$ anions formed from $C_{60}Cl_{24}$ is by an order of magnitude lower that the intensity of signals from the $C_{60}Cl_{27}^-$ anions formed from the

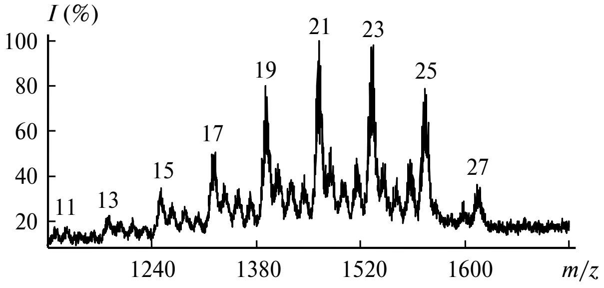

Fig. 2. Mass spectrum of negative ions of a mixture of chlorofullerenes with the average content <24 Cl atoms per C_{60} molecule; figures in curves indicates the number of Cl atoms.

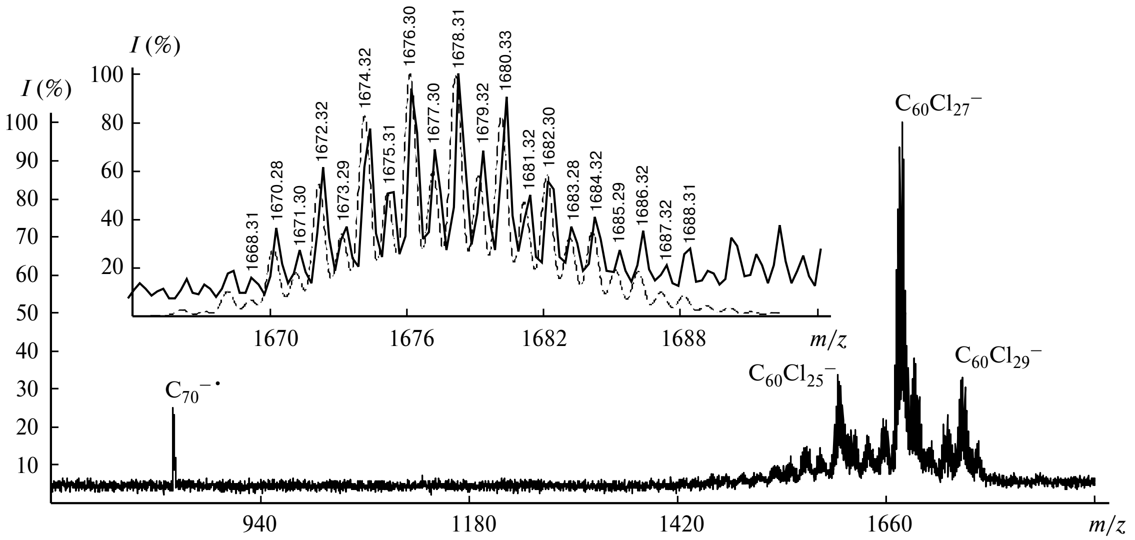

Fig. 3. Mass spectrum of negative ions in $C_{60}Cl_{24}$ with a small admixture of higher chlorides. The peak with m/z 840 corresponds to the radical anion of fullerene C_{70} added to the sample for internal calibrating. The insert shows the correspondence between the experimental (solid curve) and theoretical (dotted curve) isotope distribution for the $[C_{60}Cl_{27}]^-$ anion (resolution 2500).

$C_{60}Cl_{28}$ molecules, although the content of the latter in the sample is insignificant. Below we propose the explanation of these results as a manifestation of the suppression effect.

As known[8] for a mixture of several compounds, protonated molecular ions corresponding to a compound with the maximum proton affinity predominate in the spectrum. In our case, the electron affinities of the analyzed compounds cannot be compared directly, because dissociative anions are formed instead of molecular ions. For the same reason, ion-molecular equilibrium in a laser desorption beam can hardly exist. Therefore, one should compare the reaction rates of dissociative electron trapping

$$C_{60}Cl_{28} + [M]^{\cdot -} = [C_{60}Cl_{27}]^- + MCl \text{ (or } M + Cl^{\cdot}), \qquad (1)$$

$$C_{60}Cl_{24} + [M]^{\cdot -} = [C_{60}Cl_{23}]^- + MCl \text{ (or } M + Cl^{\cdot}), \qquad (2)$$

where M is the matrix molecule.

According to the Bell—Evans—Polanyi (BEP) principle, the reaction rate correlates with its enthalpy: for a series of similar reactions, the activation energies depend linearly on the enthalpy values. The ratio of reaction rates (1) and (2) depends similarly on the enthalpy of the exchange reaction

$$C_{60}Cl_{28} + [C_{60}Cl_{23}]^- = [C_{60}Cl_{27}]^- + C_{60}Cl_{24}, \qquad (3)$$

or in the general case,

$$C_{60}Cl_n + [C_{60}Cl_{m-1}]^- = [C_{60}Cl_{n-1}]^- + C_{60}Cl_m. \qquad (4)$$

It can be expected that the yield of anions of different composition depends on the thermodynamic characteristics of reaction (4), *i.e.*, the higher the reaction enthalpy, the higher the difference in the activation barriers and reaction rates of formation of the $[C_{60}Cl_{m-1}]^-$ and $[C_{60}Cl_{n-1}]^-$ anions. Thus, the system should correspond to some intermediate state between two ultimate cases. The first of them assumes that the activation barriers are equal, which should result in equal ratios between concentrations of anions and neutral species for all components. The second case corresponds to the quasi-equilibrium distribution of products of hypothetical reactions (3) and (4). Since these reactions are improbable to occur in the gas phase and reactions (1) and (2) are hardly reversible, a similar quasi-equilibrium state can be only of kinetic nature due to the difference in rates of formation of anions of the respective composition.

The entropy contribution to the free energy of isomolar reactions similar to (3) and (4) is usually much lower than the enthalpy contribution. We estimated the latter for reaction (3) using the DFT quantum-chemical calculation. Molecular structures for participants of the reaction were chosen from the known experimental data[2,4,9]; the geometric parameters of all species involved in the reaction were optimized by the Priroda program[10] using the PBE exchange-correlation function and a three-exponential basis set of atomic orbitals.[11] Thus determined enthalpy of reaction (3) is -50 kJ mol^{-1}. This value is sufficient to explain a substantial suppression of the signal of $C_{60}Cl_{23}^-$ when the composition of the system is close to quasi-equilibrium. The remarkable negative enthalpy is, probably, a consequence of a higher stability of the $C_{60}Cl_{27}^-$ anion, which contains, unlike $C_{60}Cl_{23}^-$, two benzene-like rings and the aromatic cyclopentadienyl anionic fragment. The high relative content of the

$C_{60}Cl_{29}^-$ and $C_{60}Cl_{25}^-$ anions is due, most likely, to similar factors.

It should be mentioned in conclusion that MALDI analyses of chlorofullerenes provide patterns that are rather difficult for interpretation. A trivial case is rather often: an overestimated content of admixtures $C_{60}Cl_n$ with $n < 24$ due to thermal dissociation of the starting compound upon laser desorption. In addition, as shown in the present work, an opposite situation is possible: an overestimated content of compounds with $n > 24$ due to the suppression effect. For dissociative trapping of a matrix electron, the equilibrium state seems improbable. However, this situation can be considered in the framework of the kinetic model based on the BEP principle, which assumes a correlation between the reaction rate and enthalpy. A similar approach, which uses the thermodynamic characteristics of the substances under study but requires no equilibrium in the system, can be applied to the formation of protonated ions and molecular anions. In a specific experiment considered in this work, the quasi-molecular ions of the main component are suppressed by the $C_{60}Cl_{27}^-$ anions containing the cyclopentadienyl fragment with high electron affinity.

The authors thank Professor M. Linscheid (Humboldt University) for a kind opportunity to use a VOYAGER-DE instrument.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 03-03-04006) and the German Research Society (Grant KE 489/20-1).

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Received February 14, 2005