

MASS-SPECTROMETRIC STUDY OF SINGLE-WALLED CARBON NANOTUBES MODIFIED BY ALIPHATIC AMINES

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Abstract

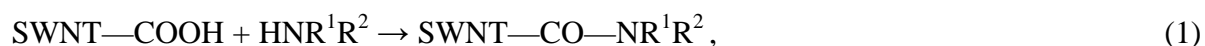
The gas-phase derivatization procedure was employed for direct (i.e., without chemical activation of terminal carboxylic groups) amidization of oxidized single-walled carbon nanotubes (SWNTs) with simple aliphatic amines. The procedure includes treatment of SWNTs with amine vapors under reduced pressure and temperature of 160-170°C. Applicability of temperature-programmed desorption mass spectrometry for chemical characterization of the derivatized SWNTs was analyzed. Heating of the amine-treated SWNTs at temperature >200°C causes cleavage of alkenes from the amine residues: nonene and pentene are formed in the case of nonylamine and dipentylamine, respectively.

Introduction

In the studies of interaction of carbon nanotubes (NTs) with organic compounds, amines gained a special attention [1-3]. In turn, the most extensively explored is the formation of amide derivatives between carboxylic groups on oxidized NT tips and long-chain amines [1-3]. The reaction is currently performed through a chemical activation of the carboxylic groups with thionyl chloride or carbodiimides in an organic solvent medium [1-3].

A decade ago we performed systematic studies on the use of the gas-phase chemical derivatization for the synthesis of chemically modified silicas, mainly for liquid chromatography applications [4-6]. However, decreasing the pressure to a moderate vacuum and, on the other hand, increasing the temperature >150°C provided efficient formation of the chemically bonded surface derivatives. In particular, the reaction between silica-bonded aminoalkyl groups and vaporous carboxylic acids to form surface amides proceeds smoothly under 150-180°C without chemical activation of the carboxylic groups.

With the above advantages of the gas-phase derivatization in mind, in the present study we have attempted to apply this procedure to oxidized SWNTs containing carboxylic groups on their tips, in other words, to verify whether the amide derivatives can be synthesized directly according to the following general scheme:



where HNR^1R^2 is an aliphatic amine. Nonylamine, dipentylamine, ethylenediamine and propylenediamine (Aldrich), SWNTs from MERC were used.

Experimental

Temperature-programmed desorption mass spectrometry (TPD MS) measurements were performed using a custom-made system. The system was based on a MX-7304A mass spectrometer (Sumy, Ukraine) with a mass range of 1-400 Da and sensitivity of 10^{-8} g.

Results and Discussion

Looking for spectroscopic methods which could be more informative for chemical characterization of SWNTs—amine systems, we tested temperature-programmed desorption mass spectrometry, which is widely used to study organic groups and molecules on inorganic adsorbent surfaces [7-9] including carbon materials [10]. The first feature found in the mass-spectra of SWNTs gas-phase treated with nonylamine is the series of hydrocarbon peaks appearing starting with temperatures of ca. 200°C (Fig. 1, *a*) at m/z 27 (C_2H_3), 29 (C_2H_5), 41 (C_3H_5), 42 (C_3H_6), 43 (C_3H_7), 55 (C_4H_7), 56 (C_4H_8), 57 (C_4H_9), 67 (C_5H_7), 69 (C_5H_9), 70 (C_5H_{10}), 71 (C_5H_{11}), 79 (C_6H_7), 81 (C_6H_9), 83 (C_6H_{11}), 84 (C_6H_{12}), 85 (C_6H_{13}), 97 (C_7H_{13}), 98 (C_7H_{14}), and 99 (C_7H_{15}). Thermograms (i.e. plots of peak intensities vs. temperature) for all of these peaks have a similar shape; they pass through a maximum at ca. 325°C (for example, Fig. 1, *b* shows thermograms for selected peaks at m/z 42, 43, 55, 57, and 69), and total disappearance of the hydrocarbon fragments is observed at ca. 400°C. No hydrocarbon peaks were found in TPD mass-spectra of SWNTs without amine treatment, recorded for comparison under the same conditions, in the same temperature interval. Taking into account consistence in their behavior, one can conclude on a common origin of the hydrocarbon fragments. Moreover, by searching for similar mass-spectra we found that both the mass numbers and peak intensity distribution correspond to nonene. The formation of nonene can be easily explained by pyrolysis of nonylamide terminal groups in SWNTs according to the following scheme:

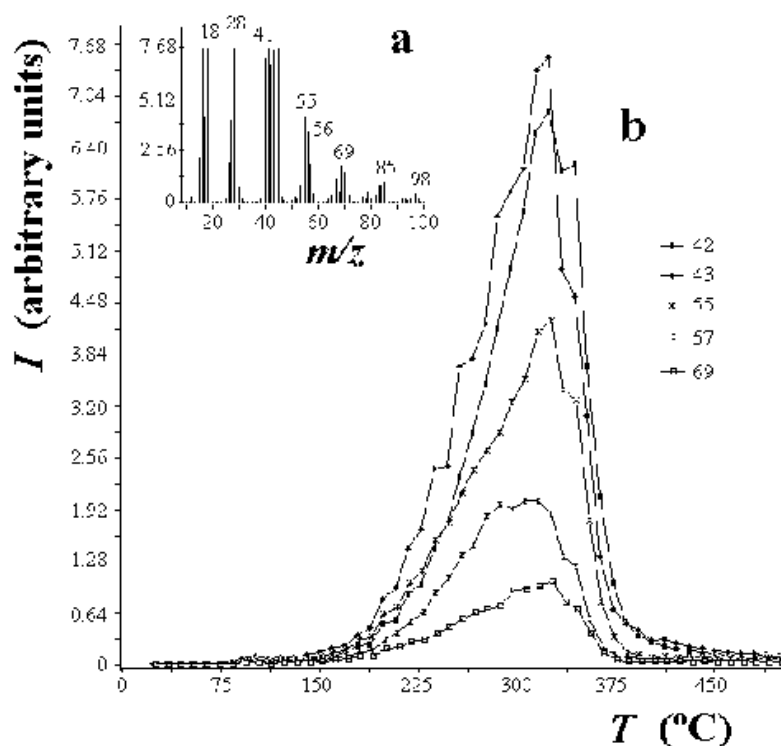
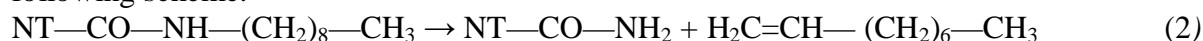


Fig. 1. (*a*) - TPD mass-spectrum of volatile products evolved at 325°C from SWNTs gas-phase treated with nonylamine; (*b*) - experimental thermograms for selected hydrocarbon peaks at m/z 42, 43, 55, 57, and 69.

Apparently, nonylamine molecules firmly adsorbed by SWNTs decompose in a similar way, forming nonene and ammonia. The presence of two forms of nonylamine can be confirmed by the following results. For a detailed analysis of thermal evolution of the hydrocarbon fragments we selected the peak at m/z 43, as one of the most abundant and illustrative peaks. According to the analytical procedure described in [9], for this peak we plotted logarithm of desorption rate k as a function of inverse temperature $\tau=(KT)^{-1}$, supposing first, second and third reaction order (Fig. 2). The dependence appears to be linear for first-order reaction. The calculated values of activation energy and pre-exponential factor ($E=79.6 \text{ kJ mol}^{-1}$ and $k_0=10^5 \text{ s}^{-1}$, respectively) are very low, suggesting existence of activation energy distribution for the process of destruction of the nonylamine species. An attempt to fit the dependence observed by rectangular distribution on activation energies [8] gave unsatisfactory results.

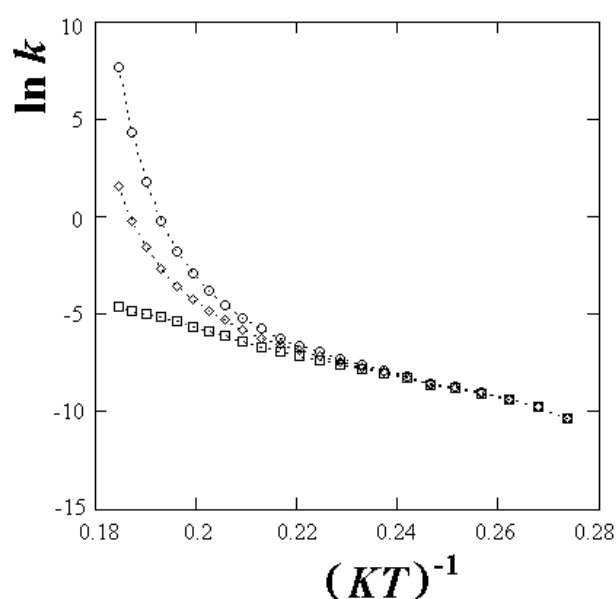


Fig. 2. Logarithm of desorption rate k for three values of reaction order (\square - first order, \diamond - second order, \circ - third order) as a function of inverse temperature $\tau=(KT)^{-1}$, calculated from Eqns (6), in [9]. Temperature dependence is linear for first-order reaction; values of activation energy E and pre-exponential factor k_0 : $E=79.6 \text{ kJ mol}^{-1}$, $k_0=10^5 \text{ s}^{-1}$.

The reason becomes clear if to consider shape of the thermodesorption curve (for m/z 43 as well as for other hydrocarbon peaks): it is noticeably asymmetric. A good agreement with the experimental curve was obtained for two activation energies, that is admitting the existence of two types of nonylamine species in SWNTs, with $E_1=81$ and $E_2=93.5 \text{ kJ mol}^{-1}$ (Fig. 3). Nonylamine physically adsorbed on SWNTs due to strong hydrophobic interactions (second thermodesorption maximum at ca. 320°C and higher abundance of hydrocarbon decomposition products). TPD—MS method was able to provide a useful information of interaction of gaseous diphenylamine with oxidized SWNTs. In some respect, its behavior is similar to that of the nonylamine sample. The mass-spectra (Fig. 4, *a*; 252°C as an example) contain a series of peaks due to hydrocarbon fragments, however the highest mass number detected was equal to 70. This peak, as well as the peaks at lower m/z , corresponds to pentene (molecular weight of 70): this identification was done by searching in the Wiley 138K Mass Spectral Library [11]. The formation of pentene can be explained by

thermal decomposition of the dipentylamide groups on the SWNT tips, by analogy with the previous case (reaction 2):

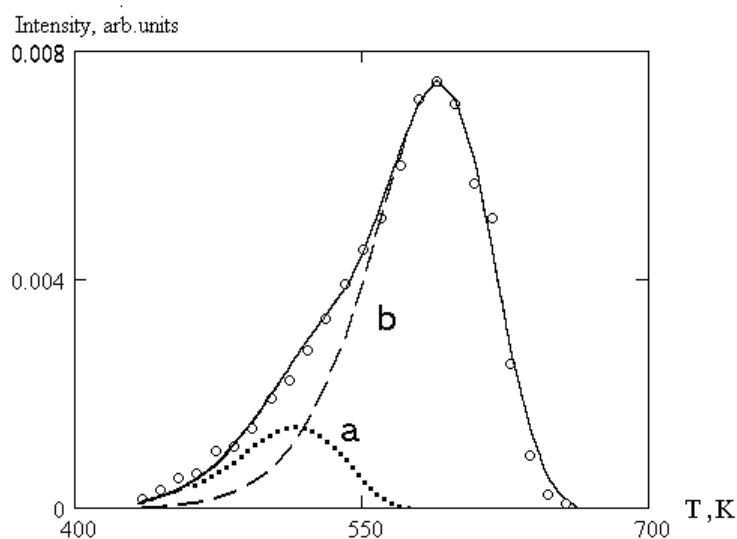
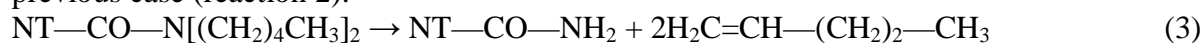


Fig. 3. Experimental thermogram (solid line) for the peak at m/z 43 for SWNTs gas-phase treated with nonylamine as a superposition of two first-order effects: (a) - $E_1=81$ and (b) - $E_2=93.5$, $k_0=10^{5.8} \text{ s}^{-1}$.

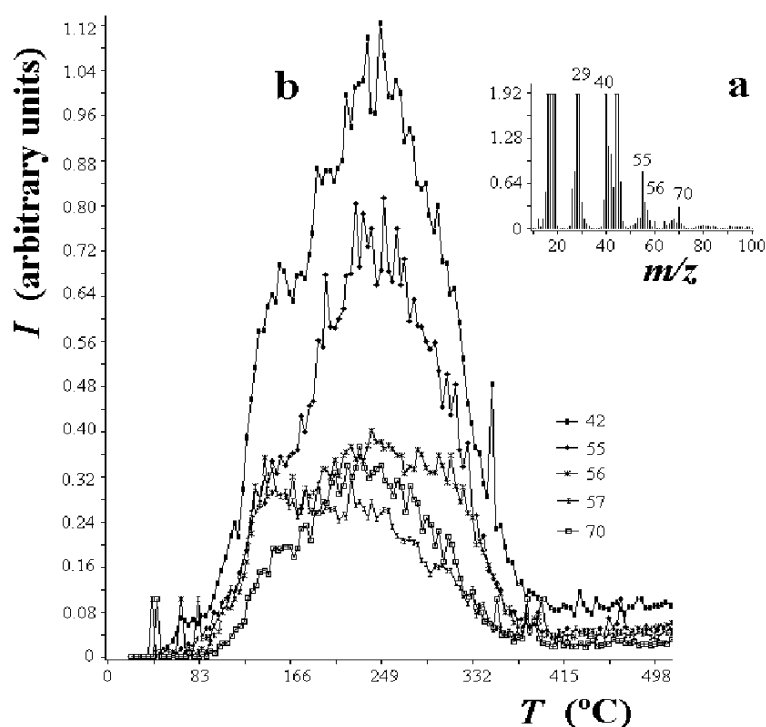


Fig. 4. (a) – TPD mass-spectrum of volatile products evolved at 252°C from SWNTs gas-phase treated with dipentylamine; (b) - experimental thermograms for selected hydrocarbon peaks at m/z 42, 55, 56, 57, and 70.

Thermodesorption curves (Fig. 4, b) for different hydrocarbon peaks have similar profiles. However, a big difference between two samples is that the curves are symmetric for the dipentylamide derivative. Their maxima were found at ca. 250°C: this approximately coincides with the first maximum for the nonylamine sample. Evolution of the hydrocarbon species ceased at <400°C. Estimation of peak intensities in the mass-spectra (sample size and detector sensitivity were kept the same in all the experiments) shows that organic contents in the present cases are lower by 0.5-1 order of magnitude as compared to the nonylamine sample. This fact agrees well with our supposition on the presence of a large fraction of physically adsorbed nonylamine in the first sample. Dipentylamine adsorption in a similar way cannot be completely denied; however fraction of the physisorbed species is incomparably lower.

Rather surprising was the absence of any hydrocarbon fragments in TPD mass-spectra of the SWNT samples treated with vaporous ethylenediamine and propylenediamine under the same (and even more harsh, up to 220°C) temperature conditions. Chemical inertness of aliphatic amino groups in these compounds is deemed totally impossible. The only remaining explanation is that the terminal amide species formed undergo further *in situ* chemical transformations and cleave off the SWNT tips. An argument on its favor is the formation of a colorless sticky (apparently polymeric) substance on the upper, cold wall of the reactor. This finding is of special interest for us, and will be studied in more detail in the future.

Conclusions

Temperature-programmed desorption mass spectrometry can provide an additional information on chemical state of amines in SWNTs. Heating of the amine-treated SWNTs at temperature >200°C causes cleavage of alkenes from the amine residues: nonene and pentene form in the case of nonylamine and dipentylamine, respectively. For the short-chain amine (dipentylamine), only one chemical form was detected, whereas two forms (amide and physically adsorbed ones) can be distinguished for the SWNTs treated with nonylamine. The contents of physically adsorbed nonylamine is about one order of magnitude higher than the amide contents.

References

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