

FREE RADICAL HALOINATION OF CARBON NANOMATERIALS AT LOW TEMPERATURES

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Introduction

One of the leading tendencies in chemistry of nanomaterials is their modification for obtaining new properties. Halogenation as one of efficient methods of modification is of great interest because both chlorine- and fluoro- derivatives should serve molecular intermediates for further modification. Chemical transformations of the attached functional groups give the base for the creation of principally new spatial structures based on carbonic nanomaterials.

Previously we have investigated solid phase halogenation reactions forming free radicals at low temperature (30-200K) which proceed under direct interaction of molecular chlorine and fluorine with polymeric materials. It has been shown that halogenation reactions are chain ones and they efficiently produced free radicals. The initiation stages were considered in the framework of model of multi-center reactions in polymolecular complex with participation of molecular chlorine and fluorine [1, 2]. These methodical approaches developed for investigation of solid phase halogenation reactions of polymeric systems, have been used in present work to reveal the extreme reactivity abilities of nanomaterials at low temperatures and to investigate by ESR and IR spectroscopy methods as well as by methods of elemental and gravimetric analysis of processes of low-temperature halogenation and fluorination of fullerenes C_{60} , single- and multi-wall nanotubes, nanofibres etc. and for their functionalization to obtain appropriate precursors.

Results and Discussion

Fullerene demonstrate inherent paramagnetism in ESR spectra as narrow singlet line with width $\Delta H=0.2$ mT and $g=2,002$ (Fig.1, spectrum 1), sometimes additional singlet at $g=1.998$ appears (spectrum 2). These paramagnetic centers (PMC) can be caused by structural defects or by remains of synthesis or refining [3]. Their concentrations for different fullerenes are $3 \times 10^{17} - 4 \times 10^{15}$ spin/g. During the contact of C_{60} with molecular fluorine at 77K new signal with $\Delta H=1,7$ mT and $g=2,0023$ arises, another narrow slight signal can be seen in its central part (spectrum 3). The new signal in the

contrast to inherent PMC signal is not saturate even at microwave power as high as 5,0 mW and it can be reliably distinguished (spectrum 4). The PMC density grows for the account of fluorination up to 3×10^{19} spin/g. The PMC thus obtained possess high stability and both their number and spectrum shape do not change under heating to 373K.

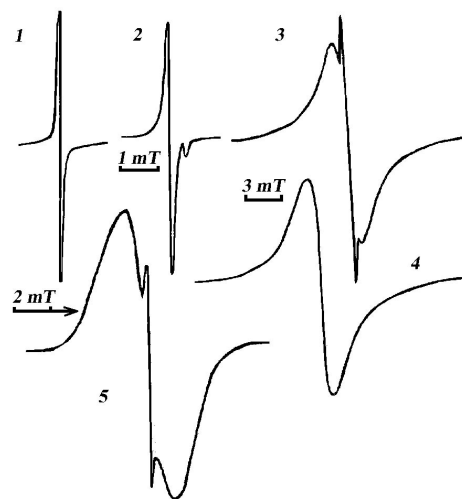


Fig.1. The ESR spectra of fullerene C_{60} (1, 2), and that fluorinated (3, 4) and chlorinated (5) at 77K.

Unlike the fluorine interacting with practically any type of chemical bonds the molecular chlorine at low temperature selectively interacts with double bonds of olefin series. To overcome the high activation energy for common chlorination the UV light has been applied to dissociate molecular chlorine to atoms.

Necessary condition for chlorine atoms chemical reaction with solid nanomaterials was the samples preliminary annealing in liquid chlorine during several hours, then they were subjected to UV radiation ($\lambda \geq 360$ nm) at 77 or 200K. In the ESR spectra arisen at the free radical driven fullerene C_{60} chlorination presented the singlet lines with different width ($\Delta H=1.5-2,7$ -mT, $g=2.000$), the last is possibly connected with variations in the conditions of preliminary processing and in the duration of their exposition to UV radiation (Fig.1, spectrum 5). The singlet lines of fluorinated fullerene can be assigned as PMC on conjugated molecular systems that

represent fullerene accepted several chlorine atoms. The fact of chlorine presence in conjugated system is evidenced as well by the weakening of saturation effects in ESR signal of chlorinated sample in comparison with the signal belonged to pure C_{60} . The last is the consequence of both the strong spin-lattice coupling in chlorine containing PMC and the growth of the spin-lattice relaxation rate.

In dependence of chlorination conditions the PMC densities were 7×10^{16} – 1.3×10^{18} spin/g (PMC background density was 4×10^{15} spin/g and $\Delta H = 0.2$ mT, $g = 2.002$). Unlike PMC in fluorinated samples the chlorinated ones are unstable and their density drops 10 – 15 times under heating from 250 to 400 K.

Gravimetric and elemental analysis lead to the following brutto-formula for the products of fullerene chlorination $C_{60}Cl_n$ ($n = 2 \div 8$). The broad bands in IR spectra (Fig.2) close to characteristic vibrations for C–Cl bonds (frequencies 885, 850 and 808 cm^{-1}) evidenced the presence of the mixture different isomers in the sample [4].

The hydrocarbon chlorination reactions usually display the radical-chained character of their mechanisms. Such a mechanisms can be suggested as well for low temperature photoinduced chlorination of carbon nanomaterials. The kinetic chain length in this process is as high 3×10^4 – 10^6 (for chlorides of $C_{60}Cl_2$ and $C_{60}Cl_8$ compounds correspondingly).

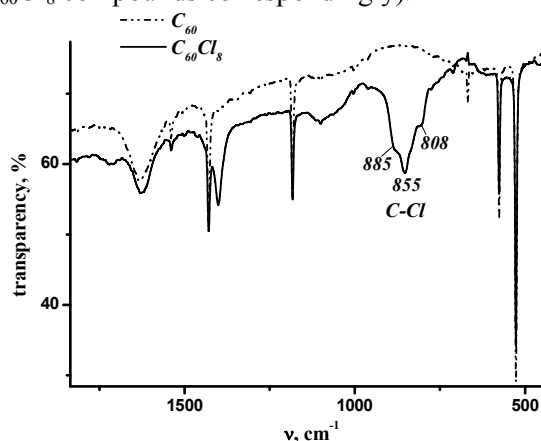


Fig.2. IR spectra of chlorinated fullerene.

Elemental analysis of chlorinated samples of carbonic nanofibers and multiple wall nanotubes revealed that the abundance of chlorine in compounds obtained is 5,8 and 1,3 mass. %, respectively.

Conclusion

Thus, for the first time it is shown that carbonic nanomaterials (fullerene, single- and multiwall nanotubes, nanofibers) demonstrate high activity at cryogenic conditions (77 K) in reactions of chain halogenation (F_2 , Cl_2) with kinetic chain length up to 10^4 – 10^5 . The ESR spectra of active free-radical intermediates were recorded. The presence of vibration bands of C–Cl bonds in products has been indicated by IR method. For the first time chain fluorination of carbonic nanofibers, mono- and multiwall nanotubes has been performed at low temperatures.

References

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