

The Potentialities of Spin Chemistry Methods in the Investigations of the Elementary Acts of Complex Reactions Including Biologically Relevant Processes

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Spin chemistry is an area of chemistry of radical reactions where the rate and direction of the reaction depend on electron-nuclear interaction in paramagnetic precursors of products. There are several physical methods based on this phenomenon. CIDNP and magnetic field effects are the most popular among them.

CIDNP phenomenon consist in the appearance of unusual signals (enhanced absorption or emission) of the products of radical reaction detected in the NMR spectra. These signals result from the abovementioned electron-nuclear interaction. Analysis of CIDNP effects allow to extract the information about the multiplicity of reactive state, structure and reactivity of free radicals.

Magnetic field effect manifests itself as the influence of the external magnetic field on reaction rate and yields of products. At present, spin chemistry method (CIDNP and magnetic field effect) are one of the most perspective physical methods of the investigation of structure and reactivity of short-lived (from nano- to microsecond) paramagnetic intermediates of chemical reactions in solution. This conclusion is fully applicable to the biologically relevant processes, too, since a lot of them include free radical stages.

First part of this presentation will be devoted to the photoinitiated interaction of biologically relevant molecules — carotenoids with electron donors and acceptors. CIDNP method has been extremely useful when studying its phototransformations (including photoisomerization). We have managed to elucidate the role of the single electron transfer process and have demonstrated the participation of the paramagnetic particles in the processes of cis-trans photoisomerization of beta-ionone, alfa-pyrane, all-trans-retinal and other carotenoids.

It is well known that organic derivatives of 14 group elements (Si, Ge, Sn) show up significant biological activity. Good example are the organosilicon compounds in the hypervalent state, silatranes. There are also organogermanium species demonstrating significant antitumor activity.

Heavy carbene analogs (silylenes, germylenes, stannylenes) — active short-lived particles, that are used for the insertion of 14 group elements into the organic compounds. The second part of this report represents the latest results of the investigations of photolysis of 7,7'-dimethyl-7-sila(germa)norbornadiene (I) — convenient source of heavy carbenes (dimethylsilylene (DMS) and -germylene (DMG)) by means of CIDNP and magnetic field effects. It has been found that DMS and DMG result from element-containing biradical. Heavy carbenes analogs obtained in the excited triplet state may undergo the conversion into singlet (ground) state in the bulk or enter the reaction with scavengers. There are two kinds of reaction detected by means of spin chemistry method: excited triplet state of DMS reacts with thiocycloheptene, CCl_4 , and I; the reaction of excited triplet state of DMG are only observed in the presence of thiacycloheptyne. Both heavy carbenes react with $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$, $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$, CH_2Cl_2 , $(\text{CH}_3)_3\text{SnCl}$ in singlet states.

DMS react with I in ground singlet state too. The main products of both reactions — tetraphenylphenylene (TPN) and tetramethyldisilabicyclooctadiene derivatives are formed via biradicals. Biradicals with two silicon atoms in initial triplet and singlet state are formed by addition of DMS to I. Magnetic field effect on TPN yield in this reaction has been recently detected. The analysis of CIDNP and magnetic effects data has allowed one to demonstrate the formation of short-lived complexes between DMS and PPh_3 , as well as those between biradicals and oxygen.

Financial support of the Russian Foundation (grants No.97-03-33810, No 98-03-32969), CRDF(grants No RC1-175, RC1-348) and INTAS (grant No 1R-97-1658) is gratefully acknowledged.