

Molecular modelling of pollutants interactions in environment

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We are conducting the investigations to the forms and structure of organic pollutants in environment, their transformation under the action of different factors: pH, temperature, time, presence of the same pollutants, variations of concentrations, influence of the aggressive media, etc. The methodology of investigations is based on multifactor analysis of stereo chemical parameters of the compounds interaction as well as their physical and chemical characteristics. With this end in view the following approach was used:

- *experimental modelling* of chemical transformations on a laboratory scale; recording the response with physical devices; elucidation of structure of the initial compounds and products of their transformation;
- *computer modelling* of behavior of the compounds using quantum chemical calculations. That makes it possible to obtain stereo chemical and thermodynamical characteristics of the molecules and their complexes, make theoretical rationalization of their reactivity, predict properties and behavior.

The data demonstrated the possibility of controlling the transformations. That may have an important theoretical importance for the study of structure of the matter. Especially estimable practical perspective: formation of new materials showing unexpected properties and resolve environmental issue.

Introduction

The key problem in the organization of environmental safety system involves the elaboration of scientific approach to ecological regulation of anthropogenic impact on environment. Ecological regulation is based on maximum permissible concentrations (MPC) of the pollutants¹. Currently the drawbacks of MPC regulation are subjected to criticism, because the MPC system is properly anthropocentric and ineffective for the protection of ecosystems². Concentration of the pollutants does not reflect:

- toxicological load on ecosystems;
- accumulation of the compounds as well as synergism and antagonism processes;
- emergency principle;
- interaction of the compounds under effect of different physical and chemical factors.

The regulation term MPE (maximum permissible emissions) has been proposed as a general index for vast territories. It does not also take into consideration the behavior of the pollutants in geosystems. Rigorous scientific approach to the evaluation of the pollutants effect on state of environmental objects and living organisms should be based on norms, which are based on geochemical principles and account for the interrelations and interactions of various compounds, such as the known transformations of phenols into hydroquinones or mercury into methyl mercury and dimethyl mercury in atmosphere. In addition, the pollution of objects by some elements must be considered bearing in mind their substitution in ecosystems for the corresponding geochemical analogs, for example, Ca → Sr, Ba and S → Se, etc.

Results of analysis of the problem

The analysis of the state of the art has shown that:

- the behavior and transformation of the pollutants (especially organic ones) in the environment is not practically studied;
- there is no common approach to the development of ecological regulations;
- an analytical control of specific pollutants may involve the method errors leading to the lost or ignorance of the other compounds content;
- incorrect approach results in the working out the ecological standards, which are inadequate with respect to the processes of the compounds transformation;
- ecological evaluation of the technologies does not take into account the transformations of chemical compounds, which may afford more toxic products than the initial pollutants;
- the development of the system of integral parameters of anthropogenic action on ecosystems is in the stage of results accumulation;
- the study of properties, migration and transformation of the pollutants in geosystems is in the search mode and has no system approach;
- the observed process of accumulation of critical mass of knowledge and results in this field is likely to bring about the review of the existing notions on the behavior of the environmental pollutants;
- scientific community realize the urgency and importance of the obtaining the information related to dynamical behavior of the pollutants in geosystems.

We are conducting the careful investigations dedicated to the forms and structure of organic pollutants in environment. Particular attention is given to their transformation under the action of different factors: pH, temperature, time, presence of the additional pollutants, variations of their concentrations, influence of the aggressive media, etc.

Methods of investigations

The methodology of investigations is based on multifactor analysis of stereochemical parameters of the elements (compounds) interaction as well as their physical and chemical characteristics. To reach this goal we have used the approach, which includes:

- experimental modelling of chemical transformations on a laboratory scale; recording the response with physical devices; elucidation of geometrical and electron structure of the initial compounds and products of their transformation;
- computer modelling of chemical behavior of the compounds using quantum chemical calculations. Quantum chemical modelling makes it possible to obtain stereochemical and thermodynamical characteristics of the molecules and complexes, evaluate dominant structures of the compounds formed, make theoretical rationalization of their reactivity, predict properties and behavior.

Such physical and chemical methods of the molecular spectroscopy as infrared (IR) and UV VIS are the best suited for the purpose in hand³. These methods reflect adequately almost all types of molecular interactions, give due consideration for the medium impact, allow one to determine structure and stoichiometric composition of the compounds and complexes formed, observe their decomposition and dynamics of transformation, find out admixtures and appearance of new functional moieties. Besides, these methods make it possible to operate with the compounds in small concentrations (up to 10^{-6} mol/l).

Results of research

For wide series of organic compounds (more than 300 classes), containing the basic functional moieties in heterocyclic and cacyclic fragments ($>C=O$, $>C=S$, $>C=N-$, $-OH$, $>NH$, $>N-N<$, $>SO_2$, $>C=C<$, $C-O-C$, etc.), we have worked out a methodology for the obtaining the «spectrum-structure» dependences, which allows one to determine molecular composition of the unknown compounds. The dependences obtained make it possible to identify types and structures of the complexes formed with organic ligands and metals in any substrate⁴. So, for example, we have experimentally studied the behavior of hydrazine derivatives $R_1CONR_2NR_3R_4$ (strong complex forming agents and oxidants) as well as some substituted amides $R_1CONR_2R_3$ in the presence of acids. The experiments involved organic acids – phenol (PhOH, $pK_a = 9.95$), trifluoroacetic acid (TFA, $pK_a = -0.26$) and inorganic acids – gaseous and liquid phase HCl ($pK_a = -7$) (Fig. 1).

Concentration of the reagents was varied over a wide range to model the products quantity observed in the emissions, waste discharge, and atmospheric precipitations.

It has been shown that the interaction of the compounds aforementioned furnishes both linear molecular complexes of donor-acceptor type (D–A) and cyclic products. At the same time, depending on the experimental conditions new structures may exist in movable tautomeric forms. We have also observed the formation of new compounds with proton transfer, i.e. one of the key reactions proceeding in living nature. Variation of the reagents concentration ratio permits to shift the equilibrium observed in one side or another⁵.

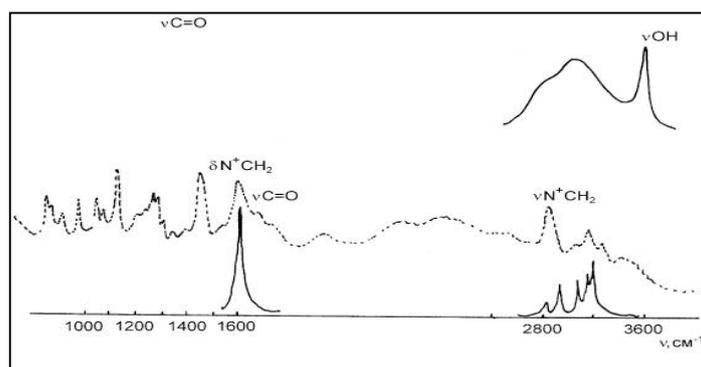


Fig. 1. The detection of amide compounds $R_1CONR_2R_3$ interaction in IR spectra:
(I) – with phenol, (II) – with HCl

These experimental data have clearly demonstrated possibility of the process control that may have an important theoretical importance for the study of organic compounds structure. Besides, this may provide a basis for the formation of new materials showing unexpected properties.

Quantum chemical (computer) modelling allows obtaining the following stereochemical characteristics of the pollutant molecules: charge distribution, electron density delocalization, ionization potential, chemical compounds formation enthalpy (DH kJ/mol) (Fig. 2).

The density of isolines shows distribution and localization of negative charge in the molecules and, thus, the ability to potential interact with other compounds in environment.

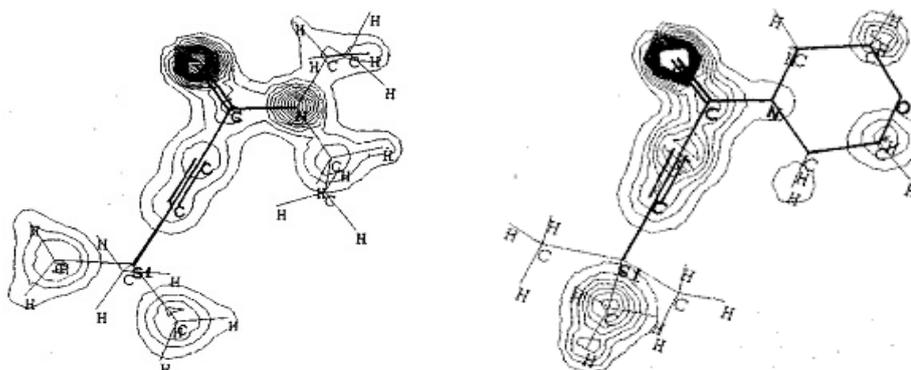
These data are used to estimate the dominant structural forms of the compounds as well as to rationalize theoretically their potential reactivity

To confirm the results the following methods have also been applied: thermal differential analysis (TDA), Raman-scattering (Raman spectroscopy), chromatography and elemental microanalysis. The results obtained will be effectively used for our further investigations related to the solution of ecological problems, studies on the behavior of pollutants and products of their transformation in environment.

Prospect of the investigation applications

The investigations aimed at the revelation of previously unknown dependences «*spectrum-structure-property*» have not only fundamental, but also very important practical significance. The results obtained can be extended to the real processes of the pollutants emissions and discharge in environment.

Fig. 2. Quantum chemical simulation data. Distribution of electron density in amides (Si – analog) according to HYPER CHEM computation



This will permit to expand the knowledge of dynamic behavior of the compounds in environment as well as to apply the data for the formulation of new concept of quality regulation of environmental objects. A huge amount of experimental data may form a basis for the development of new approaches to environmental control and determination of danger classes of the pollutants. Experimental proofs of the presence of transformation products in the emissions will stimulate the elaboration of more detail methods of analytical control and prediction.

Conclusion

The results obtained can find a practical application in the development of methods for the purification, sterilization and neutralization of industrial sewage, improvement and optimization of flotation process to extract efficiently the metals. The extension of the notions on «chemical set» of emissions and discharges on industrial enterprise will lead to the making adequate and ecologically reasonable administrative (managing) and economic decisions (cost of the pollution).

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