Developing an expert system integrated into the information portal to evaluate reactivity of organic molecules in radical reactions

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Abstract. This paper presents an approach to develop a production expert system integrated into the information portal using the fuzzy inference machine to predict reactivity of organic molecules in the radical reactions of abstraction in the liquid phase based on theoretical and experimental data. The intelligent agent technology is used to develop the expert system. The intelligent agents have their own fuzzy knowledge bases. General description of the knowledge base structure and its relations to the information portal databases are presented. Fuzzy inference models used by the intelligent agents of the expert system are listed.

1 Introduction

Knowing reactivity of organic compounds in radical reactions is an important theoretical and practical problem for basic research in physical chemistry as well as for application in chemical engineering.

Making experiments to quantify reactivity of molecules in radical reactions is expensive and hard. Quantum chemical calculations take much times and their resulting data is not sufficiently reliable. Methods of radical process simulation based on kinetic schemes require knowledge of the rate constants of elementary radical reactions. Experimental values of the rate constants of radical reactions are known only for a limited number of organic compounds in the gaseous phase [1] and liquid phase [2].

Therefore developing new approaches and tools for evaluation of reactivity of organic molecules in radical reactions based on the experimental and theoretical data is one of the most important topics of research in physical chemistry. Authors use the expert systems and fuzzy logic [3] to solve the given problem.

Papers [4,5] discuss using the expert systems and fuzzy logic in chemistry.

2 Problem formulation

Authors developed a concept of expert systems integrated into the information portal to evaluate reactivity of organic molecules in radical reactions using multiagent technology, empiric models of radical reactions and artificial neural networks [3].

In experiments reactivity of an organic molecule in a radical reaction is defined by the activation energy (E_i) or classical potential barrier (E_{ei}), which are related as follows:

$$E_{ei} = E_i + 0.5(hL\nu_i - RT) \quad (1)$$

Rate constant (k) of the chemical reaction is calculated by the Arrhenius formula:

$$k = nA_0 \exp(-E_i/RT), \quad (2)$$

where A_0 is the frequency of collisions per one reaction bond and n is the number of equireactive bonds.

Empiric models proposed in [6] evaluate classical potential barrier of radical reactions by the formulas

$$\text{if } \alpha \neq 1: \quad \sqrt{E_{ei}} = \frac{br_e}{1-\alpha^2}\left[1 - \alpha\sqrt{1 - \frac{\Delta H_e\left(1-\alpha^2\right)}{\left(br_e\right)^2}}\right] \quad (3)$$

$$\text{if } \alpha = 1: \quad \sqrt{E_{ei}} = \frac{1}{2}br_e + \frac{\Delta H_e}{2br_e} \quad (4)$$

Within the proposed empiric models of radical reactions the variables have the meaning [6].

According to the review within the model of intersecting parabolas the radical reaction of abstraction

$$H^\circ + R_1H \rightarrow RH + R^\circ_1 \quad (5)$$

is characterized by the following parameters:

1) **Enthalpy of reaction**:

$$\Delta H_e = D_i - D_f + 0.5(hL\nu_i - hL\nu_f), \quad (6)$$

where ν_i is the frequency of the stretching vibration of the breaking bond, ν_f is the frequency of the stretching vibration of the forming bond, h is Planck's constant, L is the Avogadro constant, D_i is dissociation energy of the

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breaking bond, $D_{ei} = D_i + 0{,}5hL\nu_i$, D_f is dissociation energy of the forming bond, $D_{ef} = D_f + 0{,}5hL\nu_f$.

2) **Classical potential barrier** E_{ei}:

$$E_{ei} = E_i + 0.5(hL\nu_i - RT), \quad (7)$$

is measured from the minimum of the potential curve of the breaking bond to the minimum point of the transition state. R is the gas constant, T is the thermodynamic temperature in K, E_i is the experimental value of activation energy of the radical reaction.

3) **Distance** r_e between the vertices of the potential curves in the coordinate system: the range of stretching vibrations of atoms is potential energy.

4) **Coefficients**:

$$b = \pi(2\mu_i)^{1/2}\nu_i \text{ and } b_f = \pi(2\mu_f)^{1/2}\nu_f, \quad (8)$$

describe the dependance of the potential energy from the range of stretching vibrations of atoms along the breaking (i) and forming (f) valence bond, $2b^2$ is force constant of the bond, μ_i is the reduced atom mass of the breaking bond, μ_f is the reduced atom mass of the forming bond.

5) **Coefficient**

$$\alpha = b/b_f \quad (9)$$

The main correlation ratio of the model of intersecting parabolas for the elementary act is:

$$br_e = \alpha(E_e - \Delta H_e)^{1/2} + E_e^{1/2} \quad (10)$$

The br_e value is called **kinetic parameter of the structurally similar radical reactions.**

Formula to evaluate measurement error of the potential barrier of the reaction is:

$$\Delta q = \Delta br_e \sqrt{\left(\frac{1}{1+\alpha}\right)^2 + \frac{\alpha^2}{4}\left(\frac{q}{br_e}\right)^2}, \quad (11)$$

where $q=E_{ei}^{1/2}$.

Disadvantage of such approach is that for a wide range of compounds the kinetic parameter br_e is assumed constant, which leads to considerable error in determining the classical potential barrier.

In research using the artificial neural network technology authors have attempted to escape generalized class characteristics of radical reactions. But using artificial neural networks complicates the interpretation of the derived results.

Authors' research shows that using fuzzy logic and knowledge base on its basis solves this problem.

The purpose of this paper is to propose an approach to develop expert systems integrated into the information portal to evaluate reactivity of organic molecule in radical reactions of abstraction.

The proposed approach of using multiagent technologies is the defining point of the research. This approach complies with chemistry and physics of radical reactions. Thus R+RH reactions in the liquid phase depend on the environment of the reaction. Mamdani's model of fuzzy inference functions well for hydrocarbon solvents. However in water (acid environment) a strong dependence from pH is observed, which suggests using the TSK (Takagi, Sugeno, Kang) model with polynomial dependence. Thus each intelligent agent should have its own knowledge base and make inference on the input data.

3 Problem solution

The proposed by authors approach to develop expert systems integrated into the information portal is based on using multiagent technology [3]. The expert system built in to the information portal is its active intelligent component.

During the first stage of operation the expert system should identify reagents of the radical reaction. This problem is solved using the production rules and metadata stored in the information portal thesaurus. After reagent identification their thermochemical characteristics in the knowledge base tuples are determined. Then the reaction center indexes of reactions are defined and acquired set of parameters is sent to one of the intelligent agents. The agent returns the result.

3.1 Using the knowledge base

The knowledge base of the expert system is distributed and consists of several parts: shared by all agents and linked directly to intelligent agents.

The first part of the knowledge base includes two thesauri that can be considered as domain ontologies. Thesauri contain tuples related to identification of organic molecules and radicals (atoms). They contain indexes to physical and chemical properties stored in the information portal database: bond dissociation energies and rate constants of radical reactions of abstraction. Process of reaction identification includes determination of a radical (atom), forming bond type, indexes to values of thermochemical characteristics of reagents.

Then it is checked whether database contains rate constants that satisfy the request. If such data is found in the database, it is extracted and provided to the user.

If such data is not found in the database, the shared part of the knowledge base is used to determine the reaction center index of the reaction and its characteristics. This part of the knowledge base consists of the classical production rules of the following structure:

Rule Type 1:

IF reaction class is R_1+ RH **AND** organic molecule is "alkane" **AND** molecule reaction center is «-CH_2CH_3» AND radical reaction center is «-$CH_2C^{\circ}H_2$» **THEN** kinetic parameter of reaction (br_e) = 14.93 **AND** preexponent per one equireactive bond = 10^9 **AND** α=1.0.

Then the expert system attempts to obtain thermochemical data (bond dissociation energies) from the information portal database. If such data is not found, it is proposed to the users to enter their own evaluations and the flag of high risk for the obtained results is set.

Then depending on the reaction class proper intelligent agent is chosen to calculate.

Each agent has its own knowledge base of fuzzy production rules. Depending on the reaction class, fuzzy production rules may be created using:

Mamdani's fuzzy inference machine:

RULE:

IF bond dissociation energy about "432" **AND** bond formation energy about "412" **AND** kinetic parameter of reaction about "17.3" **THEN** classical potential barrier about "40".

TSK Type 1 inference machine:

IF bond dissociation energy about "432" **AND** bond formation energy about "412" **AND** kinetic parameter of reaction about "17.3" **THEN** classical potential barrier is calculated by formulas in [7].

In case if there is no suitable intelligent agent, control is given to the agent that calculates classical potential barrier by formula (1) by the production rule:

IF bond dissociation energy about "432" **AND** bond formation energy about "412" **AND** kinetic parameter about "17.3" **THEN** classical potential barrier is calculated by formulas (3,4).

3.2 Software and technology architecture of the expert system

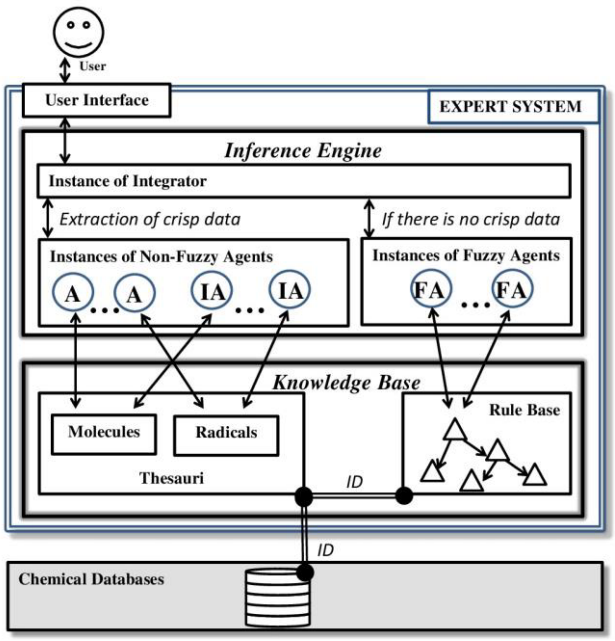

Figure 1. The architecture of the expert system

Designed originally for the portal, databases of physical and chemical properties of molecules and radicals are the factual part of thesauri for the knowledge base. Thesauri, the rule base, the chemical databases are linked identifiers that uniquely identifies the molecule, radical, or fragments thereof in the portal. If the system can respond to the user at his request with crisp data on the basis of existing knowledge, the system displays the data. If needed to predict the data, then fuzzy logic agents are invoked with attempt to predict the parameters of a radical reaction. In this case, the integrator displays the predicted parameters and their accuracy.

4 Conclusions

The proposed approach of developing the expert system integrated into the information portal to evaluate reactivity of organic molecules in radical reactions of abstractions is based on building and using the multilevel knowledge base.

The knowledge base combines shared by intelligent agents components built on the classical production rules and agents' separate knowledge bases build on various methods of fuzzy inference.

Our approach of developing the expert system integrated into the information portal combines fuzzy logic and classical production expert systems, which definitely is a new move in developing distributed applications for the use in the Internet.

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