Using fuzzy knowledge base to evaluate classical potential barrier of reactions in solutions of hydrogen atoms and hydrocarbons

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***Abstract*—**Chemical society watches closely the development of methods of artificial intelligence and applies them to solve their tasks. In particular it studies the use of applied methods of artificial intelligence for production of new knowledge from electronic chemical data collections. One of essential characteristics of chemical reactions is a classical potential barrier, which used when simulating the technological processes and creating the technology of new material development. However, its estimation is rather difficult task. Using of quantum chemical methods requires large enough resources and time. Our approach to the problem is to approximate the collected series of experimental data to solve it more efficiently. The purpose of this specific work is to combine using of empirical models of radical reactions of abstraction of hydrogen atoms with applied artificial intelligence methods, with fuzzy knowledge base, in order to approximate and then predict classical potential barrier of certain classes of such reactions on the basis of available empirical data. For this it was built fuzzy knowledge base on the basis of expert conclusions and Mamdani's fuzzy inference method was used. We have proposed a method that allows evaluating the value of classical potential barrier in the reaction of hydrogen atoms with hydrocarbons. It was shown, that the used method predicts the classical potential barrier of reactions in solutions of hydrogen atoms and hydrocarbons with high accuracy within a limited range of organic compounds.

***Keywords*—**activation energy, classical potential barrier, reaction parabolic model, rate constant, fuzzy knowledge base, Mamdani algorithm.

I. Introduction

Using methods of applied artificial intelligence, in particular, fuzzy logics and neural fuzzy systems, and methods of mathematical statistics is becoming one of the actual trends of solving applied scientific tasks in chemistry [1] and specifically in physical chemistry [2]. Currently the main directions of such research are chemical engineering [3, 4], prediction of toxicity of the compounds [5], modeling of reaction kinetics in food industry [6], evaluation of bond dissociation energy of organic compounds [7]. However, using fuzzy logics in the research of radical chemical kinetics in the liquid phase is still an open issue.

Reactivity of organic compounds of reactions of hydrogen atoms both in gas and liquid phase is very important in the research on technology process design for various chemical technologies.

The purpose of this work is to combine empirical models of radical reactions of abstraction of hydrogen atoms with applied artificial intelligence methods, in particular with fuzzy knowledge base built by experts, in order to approximate and predict classical potential barrier of such reactions.

In this paper we used Mamdani fuzzy inference method [8] based on the fuzzy knowledge base to approximate classical potential barrier of reactions in solutions of hydrogen atoms and hydrocarbons by the temperature of 296 K.

II. Material and Methods

In the middle of the last century N.N. Semenov [9] determined a linear empirical relationship between activation energy E and enthalpy ΔH of radical reactions (Polanyi-Semenov correlation).

$$E_e = E + 0.5(hL\nu_i - RT). \quad (1)$$

where ν_i – is the frequency of the stretching vibration of the breaking bond, R – is the gas constant, h – is Planck's constant, L – is the Avogadro constant, T – is the thermodynamic temperature of reaction in K.

In [10] there are two generalizations of Polanyi-Semenov empirical relationships and their interpretation within the framework of empirical model of radical reactions of abstraction:

non-linear correlation:

$$r_e = \alpha\sqrt{E_e - \Delta H_e} - \sqrt{E_e}\ . \quad (2)$$

non-linear correlation:

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$$br_e = D_{ei}^{1/2}\ln\left(\frac{D_{ei}^{1/2}}{D_{ei}^{1/2}-E_e^{1/2}}\right)+\alpha D_{ef}^{1/2}\ln\left(\frac{D_{ef}^{1/2}}{D_{ef}^{1/2}-\left(E_e-\Delta H_e\right)^{1/2}}\right) \quad (3)$$

where $\Delta H_e = D_i - D_f + 0.5\,(hL\nu_i - hL\nu_f)$ – is the reaction enthalpy including the difference between zero-point energies of the breaking and forming bond; ν_f – is the frequency of the stretching vibration of the forming bond; D_i – is the bond dissociation energy of the breaking bond; $D_{ei} = D_i + 0.5hL\nu_i$,, D_f – is the bond dissociation energy of the forming bond; $D_{ef} = D_f + 0{,}5hL\nu_f$; $b = \pi(2\mu_i)^{1/2}\nu_i$ and $b_f = \pi(2\mu_f)^{1/2}\nu_f$, μ_i parameters – is the reduced atom mass of the breaking bond; μ_f – is the reduced atom mass of the forming bond; $\alpha = b/b_f$ is the square root of the force constant ratio of the breaking and forming bond; r_e – is the displacement of the abstracted atom in the elementary act.

Within the framework of the proposed models br_e parameter in (2) is called a kinetic parameter. As it is established in [2], after processing of the experimental data by statistical methods this parameter remains almost constant for the same type of radical reactions of abstraction. Exceptions within the proposed models are reactions in water of hydrogen atoms and hydrocarbon where the activation energy of such reactions depends on the pH value.

In this work we introduce the gradation of the kinetic parameter within the range of the same class of organic compounds, for example, within alkanes we calculate by statistical methods values of this parameter for *n*-alkanes, *s*-alkanes, *t*-alkanes and cycloalkanes. By this approach the kinetic parameter of models (2) is called the empirical index of the reactionary center.

According to [2] prediction of the classical potential barrier of reactions in solutions of hydrogen atoms and hydrocarbons with known empirical indexes of the reactionary center is reduced to the solution of the equation (2) in relation to E_e.

For each specific set of thermochemical parameters and empirical indexes of the reactionary center, the classical potential barrier may be determined by the explicit formula for the first equation (2) or by the numerical method for the second equation.

However, having experimental set of the rate constants of reactions of hydrogen atoms and hydrocarbons, we can assume that the classical potential barrier of such reactions nonlinearly depends on the thermochemical characteristics of the reagents and kinetic characteristics of such reaction:

$$E_e = f(D_{ei}, D_{ef}, br_e, \alpha) \quad (4)$$

and set the task of approximation of this dependence by a feedforward artificial neural network, as in [11], or by a fuzzy knowledge base, as in this paper. We used this approach in [11] on liquid phase reactions of phenyl radical and hydrocarbons with another membership function.

III. Approximation of the Classical Potential Barrier of Reactions of Hydrogen and Hydrocarbons by a Fuzzy Knowledge Base

The experimental sample includes 51 radical reactions of hydrogen atoms and various hydrocarbons, of which 8 reactions were the testing sample. Rate constants are taken from the database of the subject-oriented scientific system on physical chemistry of radical reactions [12] and C-H bond dissociation energy were taken from [13-14].

The experimental sample has been preprocessed to avoid ambiguity in fuzzy production rules. Rate constant values are given for the temperature of 296 K. Reactions of hydrogen atom with the same reagents have been replaced with one reaction which rate constant have been determined as an average value. For example, rate constant of the reaction in hydrocarbon solution of hydrogen atom and hexane, according to the literary sources, varies from 4.7 x 10^4 to 8.4 x 10^4 l mol s^{-1}. In our calculations it is assumed 6.5 x 10^4 l mol s^{-1}.

Activation energy of reactions of hydrogen atoms and hydrocarbons has been calculated by the formula

$$E = -RT\ln\left(\frac{k}{nA_0}\right) \quad (5)$$

where A_0 – is the pre-exponential factor per one equireactive bond that equals 10^{11} l mol s^{-1}, n – is the number of equireactive bond in the molecule, k – is the rate constant of the reaction. And classical potential barrier is calculated by formula (1).

For the given experimental sample D_f =436 kJ/mol and α = 0.905 are constant. So the dependence (3) looks as follows:

$$E_e = \varphi(D_{ei}, br_{ind}) \quad (6)$$

where br_{ind} is the empirical index of the reactionary center calculated by statistic methods based on formula (2) for groups of compounds with similar reactionary centers. Empirical indexes of the reactionary center for the given sample are presented in Table I.

The fuzzy knowledge base was built by experts and includes 51 linguistic rules like (for example, for pentane)

$\boldsymbol{R}_\mathbf{i}$ **IF** D_{ei} about 430.7257 **AND** br_e about 15.81 **THEN** E_e about 55.57,

with triangular membership function to the fuzzy term G.

Mamdani's fuzzy inference method [8] has been used to approximate values of the classical potential barrier. This method is based on calculating membership functions to define the degree of compliance of the input data to every fuzzy rule. Such membership functions equal the real number α_i that defines the degree of truth of the input $A_1', A_2', \ldots, A_n'$ to the fuzzy sets $A_{i1}, A_{i2}, \ldots, A_{in}$ for each i rule

$$\alpha_i = \min_{j=1}^{n}\left[\max_{X_i}(A_j^{'}(x_j) \wedge A_{ij}(x_j))\right]. \quad (7)$$

where X_j is the range of the variables ($x_1 = D_{ei}$ and $x_2 = br_e$).

In our case the calculation of the output (classical potential barrier) consists of the following stages:

For each fuzzy rule R_i, i = 1,2, …, 85 the degree of truth is calculated by the formula

$$\alpha_i = \min\left[\max_{D_{ei}}(A_1^{'}(x_1) \wedge A_{i1}(x_1)), \max_{be_e}(A_2^{'}(x_2) \wedge A_{i2}(x_2))\right]. \quad (8)$$

TABLE I. EMPIRICAL INDEXES OF THE REACTIONARY CENTER

Compound class	*Reactionary center*	Empirical index of the reactionary center, $kJ^{0.5}\ mol^{-0.5}$
Alkanes	-C˚$(CH_3)_2$	15.92±0.05
	-C˚HCH_3	15.81±0.12
	cyclo-[C˚H$(CH_2)_k$]	16.17±0.16
Alkenes	=CHC˚H$(CH_2)_k CH_3$	16.65±0.04
	cyclo-[CH=CHC˚H$(CH_2)_k$]	17.08±0.38
Alkyl aromatic compounds	-C_6H_4C˚H_2	15.07±0.08
	C_6H_5C˚H$(CH_2)_\kappa CH_3$-	16.93
	C_6H_4C˚$(CH_3)_2$	16.21
Alcohols	C˚H_2OH	14.38
	-C˚HOH	13.90
	-CH_2C˚OH	14.33
	>C(OH)C˚H_2	15.03
Ketones	-C(O)C˚H_2	15.00
	-C(O)C˚HCH_3	15.61±0.01
	-C(O)C˚$(CH_3)_2$	16.07
	cyclo-[C(O)C˚H$(CH_2)_k$]	15.40
Ethers	-OC˚$(CH_3)_2$	14.34
	cyclo-[OC˚H$(CH_2)_k$]	14.36
	cyclo-[OC˚H$(CH_2)_k$O$(CH_2)_m$]	14.36
Acids	C˚H_2C(O)OH	14.68
	-C˚HC(O)OH	15.29±0.02
	>C˚C(O)OH	15.58

In our case the calculation of the output (classical potential barrier) consists of the following stages:

For each fuzzy rule R_i, i = 1,2, …, 85 the degree of truth is calculated by the formula

$$\alpha_i = \min\left[\max_{D_{ei}}(A_1^{'}(x_1) \wedge A_{i1}(x_1)), \max_{be_e}(A_2^{'}(x_2) \wedge A_{i2}(x_2))\right]. \quad (8)$$

For each fuzzy rule the fuzzy inference (Mamdani implication) is calculated by the formula

$$B_i^{'}(y) = \min(\alpha_i, B_i(y)). \quad (9)$$

Then the individual inferences are aggregated by the formula

$$B^{'}(y) = \max(B_1^{'}(y), B_2^{'}, ..., B_m^{'}(y)). \quad (10)$$

The resulting fuzzy set is converted into a clear value by defuzzification with the average maximum method [15].

IV. CALCULATION RESULTS

Calculation experiments have shown that classical potential barrier of reactions in solutions of hydrogen atoms and hydrocarbons may be used to predict with high accuracy its values for the wide range of such reactions based on the empirically built knowledge base.

For example, when determining a classical potential barrier of the reaction of hydrogen atom and 2-Methylpentane, for which D_{ei} = 417.2257 kJ mol^{-1} and br_e = 16.17 $kJ^{0.5}$ $mol^{-0.5}$, the fuzzy knowledge base produces value E_e = 57.29 kJ mol^{-1} that agrees with the experimental value by 296 K.

Table I shows values of classical potential barrier of reactions of hydrogen atoms and hydrocarbons E_e, calculated by the fuzzy knowledge base built on the experimental data and values calculated by the experimental data E_{exp}. As can be seen from Table II, there is a good agreement between these two sets of values.

TABLE II. COMPARING THE VALUES OF CLASSICAL POTENTIAL BARRIER OF REACTIONS IN SOLUTIONS OF HYDROGEN ATOMS AND HYDROCARBONS.

Hydrocarbon	E_e, $kJ\ mol^{-1}$	E_{exp}, $kJ\ mol^{-1}$	Δ, $kJ\ mol^{-1}$
$(CH_3)_2CHCH(CH_3)_2$	50.46	50.46	0.00
$(CH_3)_2CH(CH_2)_2CH_3$	50.48	50.48	0.00
$CH_3(CH_2)_7CH_3$	53.76	54.21	-0.45
CH_2=$CH(CH_2)_2CH_3$	38.03	37.94	0.09
cyclo-[CH(CH=CH_2)$(CH_2)_5$]	36.61	39.12	-2.51
1,4-$(CH_3)_2$-C_6H_4	32.74	32.74	0.00
$CH_3CH_2C(O)CH_2CH_3$	46.24	46.24	0.00
$CH_3(CH_2)_3C(O)OH$	44.66	44.66	0.00

V. DISCUSSION AND CONCLUSIONS

Error Δq in solution of the first equation (2) to determine value of classical potential barrier of reactions in solutions of hydrogen atoms q and hydrocarbons is according to the error theory:

$$\Delta q = \Delta br_e \sqrt{2.7 + 0.5\left(\frac{q}{br_e}\right)^2}. \quad (11)$$

Error in evaluation of classical potential barrier of radical reaction depends on error in determination of the kinetic parameter and ratio between the classical potential barrier and kinetic parameter. According to formula (5) the theoretical error of calculation is higher than that of approximation of classical potential barrier by fuzzy knowledge base built by experts, thus making the proposed approach more favorable.

In [16] feedforward artificial neural network trained by backpropagation [17] has been used to approximate classical potential barrier of reactions of hydrogen atoms and hydrocarbons. In this paper some values of empirical indexes of the reactionary center have been updated. Average calculation error in testing sample in this case is higher (about 1 kJ/mol), such as in the case of fuzzy knowledge base. However fuzzy knowledge base approximates most part of sample reactions with the error approximately equal 0. Thus, in our opinion, solution of the equation (2) using fuzzy knowledge base built by experts is more preferable.

The classical potential barrier of reactions of hydrogen atoms and hydrocarbons has been evaluated by approximation of its value by the fuzzy knowledge base built on the experimental data by experts using Mamdani's inference method.

Using fuzzy knowledge base built by experts on the experimental kinetic data and Mamdani's fuzzy inference method allows to predict within a limited range of organic compounds the classical potential barrier of reactions in solutions of hydrogen atoms and hydrocarbons with high accuracy.

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